

**Volume 31b:
Arene—X (X = N, P)**

	Preface	V
	Volume Editor's Preface	VII
	Table of Contents	XI
31.21	Product Class 21: Nitroarenes K. M. Aitken and R. A. Aitken	1183
31.22	Product Class 22: Nitrosoarenes K. Rück-Braun and B. Priewisch	1321
31.23	Product Class 23: Arenediazonium Salts P. O'Leary	1361
31.24	Product Class 24: Azoxyarenes (Di- and Monoaryldiazene Oxides) K. Rück-Braun and B. Priewisch	1401
31.25	Product Class 25: Azoarenes K. Rück-Braun, S. Dietrich, S. Kempa, and B. Priewisch	1425
31.26	Product Class 26: (Arylimino)phosphines and (Arylimino)phosphoranes M. Alajarín, C. López-Leonardo, and J. Berná	1539
31.27	Product Class 27: Arylamine <i>N</i>-Oxides and Arylaminoxyl Radicals A. Schmidt	1555
31.28	Product Class 28: Arylamines U. Scholz and B. Schlummer	1565
31.29	Product Class 29: Arylammonium Salts B. Schlummer and U. Scholz	1679
31.30	Product Class 30: <i>N</i>-Silylarylamines J. L. Chiara	1697
31.31	Product Class 31: <i>N</i>-Borylarylamines J. L. Chiara	1711
31.32	Product Class 32: <i>N</i>-Haloarylamines J. L. Chiara	1725
31.33	Product Class 33: <i>N</i>-Arylhydroxylamines A. Schmidt	1739

31.34	Product Class 34: Arylhydrazines M. Begtrup and L. K. Rasmussen	1773
31.35	Product Class 35: Aryl Azides S. Bräse, D. Keck	1827
31.36	Product Class 36: Aryltriazenes, Aryltetrazenes, and Related Compounds S. Bräse and T. Muller	1845
31.37	Product Class 37: <i>N</i>-Phosphinoarylamines M. Alajarín, C. López-Leonardo, and J. Berná	1873
31.38	Product Class 38: Cyclic Arylamines P. J. Stevenson	1885
31.39	Product Class 39: Arylphosphonic Acids and Derivatives I. B. Gorrell and T. P. Kee	1939
31.40	Product Class 40: Arylphosphinic Acids and Derivatives H.-J. Cristau and D. Virieux	1963
31.41	Product Class 41: Arylphosphine Oxides C. A. Ramsden	2035
31.42	Product Class 42: Arylphosphines and Derivatives P. J. Murphy and H. Böckemeier	2057
31.43	Product Class 43: Arylphosponium Salts and Derivatives J. C. Tebby and D. W. Allen	2083
31.44	Product Class 44: P-Heteroatom-Substituted Arylphosphines M. Alajarín, C. López-Leonardo, and J. Berná	2105
	Keyword Index	2155
	Author Index	2203
	Abbreviations	2269

Table of Contents

31.21 Product Class 21: Nitroarenes K. M. Aitken and R. A. Aitken

31.21	Product Class 21: Nitroarenes	1183
31.21.1	Synthesis of Product Class 21	1183
31.21.1.1	Method 1: Substitution of Hydrogen Using Nitric Acid Alone	1183
31.21.1.1.1	Variation 1: Using Dilute Nitric Acid	1183
31.21.1.1.2	Variation 2: Using Concentrated Nitric Acid	1185
31.21.1.1.3	Variation 3: Using Fuming Nitric Acid	1186
31.21.1.1.4	Variation 4: Using Nitric Acid on a Solid Support	1188
31.21.1.1.5	Variation 5: Using Nitric Acid in an Ionic Liquid	1190
31.21.1.2	Method 2: Substitution of Hydrogen Using Nitric and Sulfuric Acids	1191
31.21.1.3	Method 3: Substitution of Hydrogen Using Nitric and Acetic Acids	1194
31.21.1.4	Method 4: Substitution of Hydrogen Using Nitric and Acetic Acids with Additional Acid Catalysts	1196
31.21.1.5	Method 5: Substitution of Hydrogen Using Nitric Acid and Acetic Anhydride	1197
31.21.1.6	Method 6: Substitution of Hydrogen Using Nitric Acid and Acetic Anhydride–Acetic Acid	1198
31.21.1.7	Method 7: Substitution of Hydrogen Using Nitric and Trifluoroacetic Acids	1198
31.21.1.8	Method 8: Substitution of Hydrogen Using Nitric Acid and Trifluoroacetic Anhydride	1198
31.21.1.9	Method 9: Substitution of Hydrogen Using Nitric Acid and Other Acids	1199
31.21.1.9.1	Variation 1: Using Nitric and Trifluoromethanesulfonic Acids	1199
31.21.1.9.2	Variation 2: Using Nitric and Hydrochloric Acids	1199
31.21.1.9.3	Variation 3: Using Nitric and Fluorosulfonic Acids	1200
31.21.1.9.4	Variation 4: Using Nitric and Triflatoboric Acids	1200
31.21.1.9.5	Variation 5: Using Nitric Acid and Trifluoromethanesulfonic Anhydride	1201
31.21.1.9.6	Variation 6: Using Nitric Acid and Phosphorus Pentoxide	1202
31.21.1.9.7	Variation 7: Using Nitric Acid and Brønsted Acidic Ionic Liquids	1202
31.21.1.10	Method 10: Substitution of Hydrogen Using Alkali Metal Nitrates and Brønsted Acids	1202
31.21.1.10.1	Variation 1: Using Sulfuric Acid	1203
31.21.1.10.2	Variation 2: Using Acetic Acid	1206
31.21.1.10.3	Variation 3: Using Hydrofluoric Acid	1206
31.21.1.10.4	Variation 4: Using Hydrochloric Acid	1207
31.21.1.10.5	Variation 5: Using Trifluoroacetic Acid	1207
31.21.1.10.6	Variation 6: Using Boron Trifluoride Monohydrate	1208
31.21.1.11	Method 11: Substitution of Hydrogen Using Nitric Acid or Its Salts and Lewis Acid Catalysts	1209
31.21.1.11.1	Variation 1: Using Nitric Acid and Tin(IV) Chloride	1209
31.21.1.11.2	Variation 2: Using Alkali Metal Nitrates, Aluminum Trichloride, and Chlorotrimethylsilane	1210

31.21.1.11.3	Variation 3:	Using Alkali Metal Nitrates and Iron(III) Chloride or Titanium(IV) Chloride	1210
31.21.1.11.4	Variation 4:	Using Nitric Acid and Indium(III) Bis(trifluoromethylsulfonyl)amide	1211
31.21.1.11.5	Variation 5:	Using Nitric Acid and Lanthanide or Group 4 Metal Trifluoromethanesulfonates	1211
31.21.1.11.6	Variation 6:	Using Nitric Acid and Other Lanthanide Perfluoroalkanesulfonates	1212
31.21.1.11.7	Variation 7:	Using Nitric Acid and Lanthanide Arenesulfonates	1213
31.21.1.12	Method 12:	Substitution of Hydrogen Using Nitric Acid or Its Sodium Salt with Another Metal Nitrate	1213
31.21.1.12.1	Variation 1:	Using Sodium Nitrate, Hydrogen Chloride, and Lanthanum(III) Nitrate	1213
31.21.1.12.2	Variation 2:	Using Nitric Acid and Mercury(II) Nitrate with an Acid Resin	1213
31.21.1.13	Method 13:	Substitution of Hydrogen Using Nitric Acid and Mercury(II), Thallium(III), or Lead(IV) Acetate	1214
31.21.1.14	Method 14:	Substitution of Hydrogen Using Nitric Acid and Ammonium Molybdate	1214
31.21.1.15	Method 15:	Substitution of Hydrogen Using Vanadyl Nitrate	1215
31.21.1.16	Method 16:	Substitution of Hydrogen Using Transition Metal Nitrates ..	1215
31.21.1.16.1	Variation 1:	Using Iron(III) Nitrate	1215
31.21.1.16.2	Variation 2:	Using Copper(II) Nitrate	1217
31.21.1.16.3	Variation 3:	Using Chromium(III) Nitrate	1217
31.21.1.17	Method 17:	Substitution of Hydrogen Using Yttrium or Lanthanide Nitrates	1217
31.21.1.18	Method 18:	Substitution of Hydrogen Using Clay-Supported Metal Nitrates	1218
31.21.1.18.1	Variation 1:	Using Ammonium Nitrate	1218
31.21.1.18.2	Variation 2:	Using Iron(III) Nitrate	1219
31.21.1.18.3	Variation 3:	Using Copper(II) and Chromium(III) Nitrates	1220
31.21.1.18.4	Variation 4:	Using Bismuth(III) Nitrate	1220
31.21.1.19	Method 19:	Substitution of Hydrogen Using Bismuth Subnitrate and Thionyl Chloride	1220
31.21.1.20	Method 20:	Substitution of Hydrogen Using Sodium Nitrate and Phosphorus Pentoxide	1221
31.21.1.21	Method 21:	Substitution of Hydrogen Using Silver(I) Nitrate and Boron Trifluoride	1221
31.21.1.22	Method 22:	Substitution of Hydrogen Using Silver(I) Nitrate and Benzeneselenenyl Chloride	1222
31.21.1.23	Method 23:	Substitution of Hydrogen Using Copper(II) or Lead(II) Nitrate and Acetic Acid with Microwave Irradiation	1222
31.21.1.24	Method 24:	Substitution of Hydrogen Using Iron(III) Nitrate and Acetic Anhydride	1223
31.21.1.25	Method 25:	Substitution of Hydrogen Using Copper(II) Nitrate and Acetic Anhydride	1223
31.21.1.26	Method 26:	Substitution of Hydrogen Using Ammonium Nitrate and Trifluoroacetic or Trifluoromethanesulfonic Anhydride	1224

31.21.1.27	Method 27:	Substitution of Hydrogen Using Clay-Supported Metal Nitrates and Acetic Anhydride	1225
31.21.1.27.1	Variation 1:	Using Copper(II) Nitrate	1225
31.21.1.27.2	Variation 2:	Using Other Metal Nitrates	1226
31.21.1.28	Method 28:	Substitution of Hydrogen Using Transition Metal Nitrate–Dinitrogen Tetroxide Adducts	1226
31.21.1.29	Method 29:	Substitution of Hydrogen Using Ammonium Cerium(IV) Nitrate Alone	1227
31.21.1.30	Method 30:	Substitution of Hydrogen Using Ammonium Cerium(IV) Nitrate with Oxidizing Agents	1228
31.21.1.30.1	Variation 1:	Using Iodine	1228
31.21.1.30.2	Variation 2:	Using Hydrogen Peroxide	1228
31.21.1.31	Method 31:	Substitution of Hydrogen Using Ammonium Cerium(IV) Nitrate with Dehydrating Agents	1229
31.21.1.31.1	Variation 1:	Using Acetic Anhydride	1229
31.21.1.31.2	Variation 2:	Using Sulfuric Acid	1229
31.21.1.31.3	Variation 3:	Using Sulfuric Acid and an Additive	1230
31.21.1.32	Method 32:	Substitution of Hydrogen Using Ammonium Cerium(IV) Nitrate on Silica Gel	1230
31.21.1.33	Method 33:	Substitution of Hydrogen Using Acyl and Alkyl Nitrates	1231
31.21.1.33.1	Variation 1:	Using Acetyl Nitrate	1231
31.21.1.33.2	Variation 2:	Using Benzoyl Nitrate	1231
31.21.1.33.3	Variation 3:	Using 1-Alkyl-3-[(nitrooxy)carbonyl]pyridinium Salts	1231
31.21.1.33.4	Variation 4:	Using Other Acyl Nitrates	1232
31.21.1.33.5	Variation 5:	Using Propyl Nitrate on Zeolites	1232
31.21.1.33.6	Variation 6:	Using Protonated Methyl Nitrate	1232
31.21.1.34	Method 34:	Substitution of Hydrogen Using Nitroalkanes	1232
31.21.1.34.1	Variation 1:	Using Tetranitromethane	1232
31.21.1.34.2	Variation 2:	Using Nitrocyclohexadienones	1233
31.21.1.35	Method 35:	Substitution of Hydrogen Using Organic Nitrates	1234
31.21.1.35.1	Variation 1:	Using Pyridinium Nitrate	1234
31.21.1.35.2	Variation 2:	Using Urea Nitrate	1234
31.21.1.35.3	Variation 3:	Using Guanidinium Nitrate	1235
31.21.1.36	Method 36:	Substitution of Hydrogen Using Nitrogen Dioxide Alone	1236
31.21.1.37	Method 37:	Substitution of Hydrogen Using a Photochemical Reaction with Nitrogen Dioxide	1237
31.21.1.38	Method 38:	Substitution of Hydrogen Using Nitrogen Dioxide with Brønsted Acids	1237
31.21.1.38.1	Variation 1:	Using Sulfuric Acid	1237
31.21.1.38.2	Variation 2:	Using Trifluoroacetic Acid	1237
31.21.1.39	Method 39:	Substitution of Hydrogen Using Nitrogen Dioxide with Lewis Acids	1237
31.21.1.39.1	Variation 1:	Using Boron Trifluoride	1237
31.21.1.39.2	Variation 2:	Using Aluminum Trichloride	1238
31.21.1.40	Method 40:	Substitution of Hydrogen Using Nitrogen Dioxide with 18-Crown-6	1239
31.21.1.41	Method 41:	Substitution of Hydrogen Using Nitrogen Dioxide in the Presence of a Solid Support	1240

31.21.1.41.1	Variation 1:	Using Silica Gel	1240
31.21.1.41.2	Variation 2:	Using Silica Acetate	1240
31.21.1.42	Method 42:	Substitution of Hydrogen Using Nitrogen Dioxide with Oxygen	1241
31.21.1.42.1	Variation 1:	Iron-Catalyzed Reaction	1241
31.21.1.42.2	Variation 2:	Zeolite-Catalyzed Reaction	1241
31.21.1.43	Method 43:	Substitution of Hydrogen Using Nitrogen Dioxide with Ozone: "Kyodai" Nitration	1242
31.21.1.44	Method 44:	Substitution of Hydrogen Using Dinitrogen Pentoxide	1245
31.21.1.45	Method 45:	Substitution of Hydrogen Using Dinitrogen Pentoxide and Sulfur Dioxide	1245
31.21.1.46	Method 46:	Substitution of Hydrogen Using Dinitrogen Pentoxide and Sulfur Trioxide	1246
31.21.1.47	Method 47:	Substitution of Hydrogen Using Dinitrogen Pentoxide: Other Methods	1246
31.21.1.47.1	Variation 1:	Using Zeolites	1246
31.21.1.47.2	Variation 2:	Using Iron(III) Acetylacetonate	1246
31.21.1.47.3	Variation 3:	Using Zirconium(IV) Acetylacetonate	1247
31.21.1.47.4	Variation 4:	In Perfluorinated Solvents	1247
31.21.1.48	Method 48:	Substitution of Hydrogen Using Nitronium Salts and Complexes	1248
31.21.1.48.1	Variation 1:	Using Nitronium Tetrafluoroborate	1248
31.21.1.48.2	Variation 2:	Using Nitronium Hexafluorophosphate	1250
31.21.1.48.3	Variation 3:	Using Nitronium Hydrogen Sulfate	1250
31.21.1.48.4	Variation 4:	Using Nitronium Fluoride	1250
31.21.1.48.5	Variation 5:	Using Sodium Nitrite and Selectfluor	1251
31.21.1.48.6	Variation 6:	Using Nitronium Chloride	1251
31.21.1.48.7	Variation 7:	Using Nitrodiazonium Tetrafluoroborate	1252
31.21.1.48.8	Variation 8:	Using Heterocyclic <i>N</i> -Nitro Salts	1252
31.21.1.49	Method 49:	Substitution of Hydrogen Using Nitric Oxide and Oxygen ...	1254
31.21.1.50	Method 50:	Substitution of Hydrogen Using Nitrosonium Salts and Oxygen	1254
31.21.1.51	Method 51:	Substitution of Hydrogen Using Sodium Nitrite with Acids or Oxidizing Agents	1254
31.21.1.51.1	Variation 1:	Using Sulfuric Acid	1254
31.21.1.51.2	Variation 2:	Using Acetic Acid	1255
31.21.1.51.3	Variation 3:	Using Trifluoroacetic Acid	1256
31.21.1.51.4	Variation 4:	Using Ammonium Peroxydisulfate	1257
31.21.1.51.5	Variation 5:	Using Silica Sulfuric Acid	1257
31.21.1.51.6	Variation 6:	Using Trichloroisocyanuric Acid and Silica Gel	1258
31.21.1.51.7	Variation 7:	Using Sodium or Magnesium Hydrogen Sulfate and Silica Gel	1258
31.21.1.51.8	Variation 8:	Using Oxone and Silica Gel	1259
31.21.1.52	Method 52:	Substitution of Hydrogen Using Electrochemical Reactions	1259
31.21.1.52.1	Variation 1:	With Nitric Acid	1259
31.21.1.52.2	Variation 2:	With Nitrogen Dioxide	1259
31.21.1.53	Method 53:	Substitution of Lithium by Reaction of Aryllithium Reagents with Nitrogen Dioxide	1260

31.21.1.54	Method 54:	Substitution of Copper by Reaction of Phenylcopper with Nitric Acid	1260
31.21.1.55	Method 55:	Substitution of Boron by Reaction of an Arylboronic Acid with a Metal Nitrate and a Dehydrating Agent	1260
31.21.1.55.1	Variation 1:	Using Ammonium Nitrate and Trifluoroacetic Anhydride ...	1260
31.21.1.55.2	Variation 2:	Using Ammonium or Silver(I) Nitrate and Chlorotrimethylsilane	1261
31.21.1.56	Method 56:	Substitution of Silicon by Reaction of an Aryltrimethylsilane with a Nitrating Agent	1261
31.21.1.56.1	Variation 1:	Using Nitric Acid and Acetic Anhydride	1261
31.21.1.56.2	Variation 2:	Using Nitric and Sulfuric Acids	1262
31.21.1.56.3	Variation 3:	Using Nitronium Tetrafluoroborate	1263
31.21.1.57	Method 57:	Substitution of Tin by Reaction of an Aryltrimethylstannane with Nitrosyl Chloride Followed by Potassium Permanganate Oxidation	1263
31.21.1.58	Method 58:	Substitution of a Carboxylic Acid Group Using Nitric Acid ...	1264
31.21.1.59	Method 59:	Substitution of a Carboxylic Acid Group Using Nitric and Acetic Acids	1264
31.21.1.60	Method 60:	Substitution of a Carboxylic Acid Group Using Nitric Acid and 2,2'-Azobisisobutyronitrile	1265
31.21.1.61	Method 61:	Substitution of an Aldehyde Group Using Nitric and Sulfuric Acids	1265
31.21.1.62	Method 62:	Substitution of a <i>tert</i> -Butyl Group in a Calixarene or a [2.2.2]Metacyclopentane	1266
31.21.1.62.1	Variation 1:	Using Nitric and Sulfuric Acids	1266
31.21.1.62.2	Variation 2:	Using Nitric and Acetic Acids	1267
31.21.1.62.3	Variation 3:	Using Nitric and Trifluoroacetic Acids	1268
31.21.1.62.4	Variation 4:	Using Sodium Nitrate and Trifluoroacetic Acid	1269
31.21.1.62.5	Variation 5:	Using Copper(II) Nitrate and Trifluoroacetic Acid	1270
31.21.1.63	Method 63:	Substitution of a <i>tert</i> -Butyl or an Isopropyl Group Using Nitronium Tetrafluoroborate	1271
31.21.1.64	Method 64:	Substitution of a Methyl Group Using Nitric and Sulfuric Acids	1271
31.21.1.65	Method 65:	Substitution of Chlorine Using Nitric Acid	1272
31.21.1.66	Method 66:	Substitution of Chlorine Using Nitric and Acetic Acids	1272
31.21.1.67	Method 67:	Substitution of Chlorine Using Alkali Metal Nitrites	1272
31.21.1.68	Method 68:	Substitution of Bromine Using Nitric Acid	1273
31.21.1.69	Method 69:	Substitution of Bromine Using Nitric and Sulfuric Acids	1274
31.21.1.70	Method 70:	Substitution of Bromine Using Nitric and Acetic Acids	1274
31.21.1.71	Method 71:	Substitution of Bromine Using Nitric Acid and Acetic Anhydride	1275
31.21.1.72	Method 72:	Substitution of Bromine Using Sodium Nitrite and Acetic Acid	1276
31.21.1.73	Method 73:	Substitution of Bromine Using Ethyl Nitrite	1276
31.21.1.74	Method 74:	Substitution of Iodine Using Nitric Acid	1277
31.21.1.75	Method 75:	Substitution of Iodine Using Nitric and Acetic Acids	1278
31.21.1.76	Method 76:	Substitution of Iodine Using Sodium Nitrite and Sulfuric Acid	1278
31.21.1.77	Method 77:	Substitution of Iodine Using Silver(I) Nitrate	1278

31.21.1.78	Method 78:	Substitution of Sulfur by Reaction of an Arenesulfonic Acid with Nitric Acid	1278
31.21.1.79	Method 79:	Substitution of Nitrogen by Reaction of Diazonium Salts with Sodium Nitrite	1279
31.21.1.80	Method 80:	Substitution of Nitrogen by Reaction of Diazonium Salts with Sodium Nitrite and Copper Metal	1280
31.21.1.80.1	Variation 1:	Using Conventional Diazotization	1280
31.21.1.80.2	Variation 2:	Using Nitrosonium Tetrafluoroborate	1281
31.21.1.81	Method 81:	Substitution of Nitrogen by Reaction of Diazonium Salts with Sodium Nitrite and Copper(I) Oxide	1282
31.21.1.81.1	Variation 1:	Using Conventional Diazotization	1282
31.21.1.81.2	Variation 2:	Using Diazonium Hexanitrocobaltates(III)	1283
31.21.1.82	Method 82:	Substitution of Nitrogen by Reaction of Diazonium Salts with Sodium Nitrite and Copper(II) Sulfate	1283
31.21.1.82.1	Variation 1:	Using Conventional Diazotization	1283
31.21.1.82.2	Variation 2:	Using Isopentyl Nitrite	1283
31.21.1.83	Method 83:	Substitution of Nitrogen by Reaction of Diazonium Salts with Sodium Nitrite, Copper(I) Oxide, and Copper(II) Sulfate	1284
31.21.1.83.1	Variation 1:	Using Diazonium Sulfates or Chlorides	1284
31.21.1.83.2	Variation 2:	Using Diazonium Hexanitrocobaltates(III)	1285
31.21.1.84	Method 84:	Substitution of Nitrogen by Reaction of Diazonium Salts with Sodium Nitrite and Copper(I,II) Sulfite	1286
31.21.1.85	Method 85:	Oxidation of Primary Amines Using Oxygen with a Metal Catalyst	1287
31.21.1.86	Method 86:	Oxidation of Primary Amines Using Hydrogen Peroxide	1287
31.21.1.86.1	Variation 1:	With a Transition Metal Complex Catalyst	1287
31.21.1.86.2	Variation 2:	With Ruthenium(III) Chloride and a Phase-Transfer Catalyst	1288
31.21.1.86.3	Variation 3:	With Enzymatic Catalysis	1288
31.21.1.86.4	Variation 4:	With an Acetylcholine Catalyst	1288
31.21.1.86.5	Variation 5:	With a Silica Gel Supported Fluoro Ketone Catalyst	1289
31.21.1.87	Method 87:	Oxidation of Primary Amines Using Sodium Peroxide	1289
31.21.1.88	Method 88:	Oxidation of Primary Amines Using Hypofluorous Acid	1289
31.21.1.89	Method 89:	Oxidation of Primary Amines Using Nitrogen Oxides	1290
31.21.1.90	Method 90:	Oxidation of Primary Amines Using Peroxysulfuric Acid or Peroxydisulfuric Acid	1290
31.21.1.91	Method 91:	Oxidation of Primary Amines Using Sodium Perborate	1292
31.21.1.92	Method 92:	Oxidation of Primary Amines Using Sodium Peroxycarbonate	1293
31.21.1.93	Method 93:	Oxidation of Primary Amines Using Quaternary Ammonium Bromates	1293
31.21.1.94	Method 94:	Oxidation of Primary Amines Using Potassium Permanganate	1293
31.21.1.95	Method 95:	Oxidation of Primary Amines Using Potassium Ferrate	1293
31.21.1.96	Method 96:	Oxidation of Primary Amines Using Organic Peroxides	1294
31.21.1.96.1	Variation 1:	Using Dimethyldioxirane	1294
31.21.1.96.2	Variation 2:	Using a Polymer-Bound Dioxirane	1295
31.21.1.96.3	Variation 3:	Using Other Dioxiranes	1295
31.21.1.96.4	Variation 4:	Using <i>tert</i> -Butyl Hydroperoxide with a Metal Catalyst	1295
31.21.1.96.5	Variation 5:	Using Oxaziridinium Salts	1296

31.21.1.97	Method 97:	Oxidation of Primary Amines Using Organic Peroxy Acids ...	1296
31.21.1.97.1	Variation 1:	Using Performic Acid	1296
31.21.1.97.2	Variation 2:	Using Peracetic Acid	1296
31.21.1.97.3	Variation 3:	Using Trifluoroperoxyacetic Acid	1297
31.21.1.97.4	Variation 4:	Using Peroxymaleic Acid	1299
31.21.1.97.5	Variation 5:	Using 3-Chloroperoxybenzoic Acid	1299
31.21.1.97.6	Variation 6:	Using Peroxytrifluoromethanesulfonic Acid	1300
31.21.1.98	Method 98:	Oxidation of Tertiary Amines Using Trifluoroperoxyacetic Acid	1300
31.21.1.99	Method 99:	Oxidation of Hydroxylamines and Alkoxyamines Using Ozone	1301
31.21.1.100	Method 100:	Oxidation of Acetanilides Using Ozone in Oleum	1301
31.21.1.101	Method 101:	Oxidation of Nitroso Compounds Using Oxygen with a Transition Metal Catalyst	1301
31.21.1.102	Method 102:	Oxidation of Nitroso Compounds Using Aqueous Hydrogen Peroxide	1302
31.21.1.102.1	Variation 1:	With a Base	1302
31.21.1.102.2	Variation 2:	With a Transition Metal Catalyst	1302
31.21.1.103	Method 103:	Oxidation of Nitroso Compounds Using Nitrogen Oxides ...	1303
31.21.1.104	Method 104:	Oxidation of Nitroso Compounds Using Nitrous Acid	1303
31.21.1.105	Method 105:	Oxidation of Nitroso Compounds Using Nitric Acid	1303
31.21.1.106	Method 106:	Oxidation of Nitroso Compounds Using Sulfuric Acid	1304
31.21.1.107	Method 107:	Oxidation of Nitroso Compounds Using Fluorosulfonic Acid	1305
31.21.1.108	Method 108:	Oxidation of Nitroso Compounds Using Peroxysulfuric Acid	1305
31.21.1.109	Method 109:	Oxidation of Nitroso Compounds Using Chromium(VI) Reagents	1306
31.21.1.110	Method 110:	Oxidation of Nitroso Compounds Using Potassium Permanganate	1306
31.21.1.111	Method 111:	Oxidation of Nitroso Compounds Using Potassium Hexacyanoferrate(III) with a Base	1307
31.21.1.112	Method 112:	Oxidation of Nitroso Compounds Using Peracetic Acid	1307
31.21.1.113	Method 113:	Oxidation of Nitroso Compounds Using Trifluoroperoxyacetic Acid	1308
31.21.1.114	Method 114:	Oxidation of Nitroso Compounds Using 3-Chloroperoxybenzoic Acid	1309
31.21.1.115	Method 115:	Oxidation of Nitroso Compounds Using Iodosylbenzene with a Metal Catalyst	1309
31.21.1.116	Method 116:	Oxidation of Sulfimides Using 3-Chloroperoxybenzoic Acid	1309
31.22	Product Class 22: Nitrosoarenes K. Rück-Braun and B. Priewisch		
31.22	Product Class 22: Nitrosoarenes		1321
31.22.1	Synthesis of Product Class 22		1321
31.22.1.1	Nitrosation Reactions		1321
31.22.1.1.1	Method 1:	Nitrosation of Phenols by Nitrous Acid	1322
31.22.1.1.1.1	Variation 1:	Nitrosation of Phenols by Alkyl Nitrites	1325

31.22.1.1.2	Method 2:	Nitrosation of Arylamines by Nitrous Acid	1325
31.22.1.1.2.1	Variation 1:	Of Tertiary Arylamines	1326
31.22.1.1.2.2	Variation 2:	Of Secondary Arylamines	1327
31.22.1.1.2.3	Variation 3:	Of Primary Arylamines	1328
31.22.1.1.3	Method 3:	Nitrosation by Nitrosonium Tetrafluoroborate	1329
31.22.1.1.4	Method 4:	Nitrosation of Arylmetal Compounds	1331
31.22.1.1.4.1	Variation 1:	Of Arylsilanes	1332
31.22.1.1.4.2	Variation 2:	Of Arylstannanes	1333
31.22.1.1.4.3	Variation 3:	Of Arylthallium Compounds	1334
31.22.1.1.4.4	Variation 4:	Of Arylmercury Compounds	1335
31.22.1.2	Reduction of Nitroarenes		1336
31.22.1.2.1	Method 1:	Reductions with Alkyl Grignard Reagents	1336
31.22.1.2.2	Method 2:	Reduction with Metals or Metal Oxides	1338
31.22.1.2.3	Method 3:	Nucleophilic Aromatic Substitution of Nitroarenes with Concomitant Reduction	1338
31.22.1.2.4	Method 4:	Electrochemical Reduction	1339
31.22.1.2.5	Method 5:	Photochemical Reduction	1339
31.22.1.3	Oxidation of Arylamines		1339
31.22.1.3.1	Method 1:	Oxidation by Peracids	1339
31.22.1.3.1.1	Variation 1:	Using Caro's Acid	1340
31.22.1.3.1.2	Variation 2:	Using Oxone	1340
31.22.1.3.1.3	Variation 3:	Using Peracetic Acid	1341
31.22.1.3.1.4	Variation 4:	Using 3-Chloroperoxybenzoic Acid	1343
31.22.1.3.2	Method 2:	Oxidation by Hydrogen Peroxide and a Transition-Metal Catalyst	1344
31.22.1.3.2.1	Variation 1:	With Tungsten Catalysts	1344
31.22.1.3.2.2	Variation 2:	With Molybdenum Catalysts	1345
31.22.1.4	Oxidation of <i>N</i> -Arylhydroxylamines		1346
31.22.1.4.1	Method 1:	Oxidation by Iron(III) Chloride	1346
31.22.1.4.2	Method 2:	Oxidation by Sodium or Potassium Dichromate	1347
31.22.1.4.3	Method 3:	Oxidation by <i>tert</i> -Butyl Hypochlorite	1347
31.22.1.4.4	Method 4:	Electrochemical Oxidation	1348
31.22.1.5	Rearrangement Reactions		1349
31.22.1.5.1	Method 1:	Rearrangement of <i>N</i> -Nitrosoarylamines (Fischer–Hepp Rearrangement)	1349
31.22.1.5.2	Method 2:	Photochemical Rearrangement of Nitroarenes	1349
31.22.1.5.3	Method 3:	Acid- or Base-Catalyzed Rearrangements of Nitroarenes	1350
31.22.1.6	Synthesis from Other Nitrosoarenes		1352
31.22.1.6.1	Method 1:	Electrophilic Halogenation or Nitration of Nitrosobenzene	1352
31.22.1.6.2	Method 2:	Nucleophilic Aromatic Substitution Reactions of Nitrosoarenes	1352
31.22.1.6.3	Method 3:	Reactions at the Side Chains of Aryl Nitroso Compounds: Etherification of 4-Nitrosophenol	1354
31.22.2	Applications of Product Class 22 in Organic Synthesis		1355

31.23 Product Class 23: Arenediazonium Salts

P. O'Leary

31.23	Product Class 23: Arenediazonium Salts	1361
31.23.1	Product Subclass 1: Simple Arenediazonium Salts	1362
31.23.1.1	Synthesis of Product Subclass 1	1363
31.23.1.1.1	Method 1: Direct Introduction of the Diazonium Group	1363
31.23.1.1.2	Method 2: Diazotization of Primary Aromatic Amines	1364
31.23.1.1.2.1	Variation 1: Diazotization Using 2,2-Dimethylpropane-1,3-diyl Dinitrite	1364
31.23.1.1.2.2	Variation 2: Formation of Arenediazonium Salts by Diazotization in Acidic Solution	1365
31.23.1.1.3	Method 3: Reactions of Anilines with Sodium Nitrite in Acidic Media, Followed by Anion Exchange	1369
31.23.1.1.3.1	Variation 1: Use of an Inorganic Salt To Alter the Anion	1370
31.23.1.1.3.2	Variation 2: Use of an Acid To Alter the Anion	1373
31.23.1.1.4	Method 4: Diazotization of Weakly Basic Amines by Dissolution in Pyridine, Prior to Treatment with Sodium Nitrite and Sulfuric Acid	1374
31.23.1.1.5	Method 5: Diazotization of Aromatic Amines under "Anhydrous" Conditions	1375
31.23.1.1.5.1	Variation 1: Diazotization Using Alkyl Nitrites and an Acid as the Anion Donor	1375
31.23.1.1.5.2	Variation 2: Reactions Using Boron Trifluoride as the Anion Source	1377
31.23.1.1.5.3	Variation 3: Reactions Using Organic Compounds as the Anion Source	1378
31.23.1.1.5.4	Variation 4: Diazotization Using Nitrosonium Tetrafluoroborate	1379
31.23.1.1.5.5	Variation 5: Diazotization Using Nitric Oxide or Nitric Oxide and Lead(IV) Oxide	1380
31.23.1.1.6	Method 6: Synthesis and Isolation of Arenediazonium Salts by Amine Diazotization under Solvent-Free Conditions	1381
31.23.1.1.6.1	Variation 1: Diazotization with Nitrogen Dioxide Gas	1381
31.23.1.1.6.2	Variation 2: Diazotization Using Liquid Nitrogen Dioxide	1382
31.23.1.1.6.3	Variation 3: Diazotization with Nitrosyl Chloride	1383
31.23.1.1.7	Method 7: Synthesis of Arenediazonium Salts with Simultaneous Modification of Other Substituents	1384
31.23.1.1.7.1	Variation 1: With Ester Cleavage	1384
31.23.1.1.7.2	Variation 2: Diazotization and Heterocyclization	1384
31.23.1.1.8	Method 8: Synthesis from <i>N</i> -Acylarylamines Using Nitrosyl Reagents	1385
31.23.1.1.9	Method 9: Synthesis of Diazonium Salts from Imines, <i>N</i> -Sulfinylamines, Nitrosoarenes, or <i>N,N</i> -Disilylanilines with Nitrosyl Compounds	1386
31.23.1.1.9.1	Variation 1: From Benzaldehyde Arylimines and a Nitrosyl Reagent	1386
31.23.1.1.9.2	Variation 2: From <i>N</i> -Sulfinylamines and Nitrosonium Perchlorate or Nitrosonium Hexachloroantimonate	1387
31.23.1.1.9.3	Variation 3: From Nitrosoarenes and Nitrosyl Halides	1387
31.23.1.1.9.4	Variation 4: From <i>N,N</i> -Bis(trimethylsilyl)anilines	1388
31.23.1.1.10	Method 10: Synthesis from 1-Alkyl-2-aryl- or 1,2-Diaryldiazenes	1388
31.23.1.1.11	Method 11: Synthesis from Alkyl(aryl)triazenes	1389

31.23.1.1.12	Method 12: Synthesis from Other Arenediazonium Salts	1390
31.23.2	Product Subclass 2: Arenediazonium Inner Salts	1391
31.23.2.1	Synthesis of Product Subclass 2	1391
31.23.2.1.1	Method 1: Hydration of Halo- or Nitrodiazonium Salts	1391
31.23.2.1.2	Method 2: Diazotization of Aminophenols, Aminonaphthols, Aminobenzenesulfonic Acids, and Aminoarene-carboxylic Acids in Acidic Media	1392
31.23.2.1.3	Method 3: Diazotization and Oxidation of Aminoarenes in Acidic Media	1394
31.23.3	Product Subclass 3: Polymeric and Immobilized Arenediazonium Salts	1394
31.24	Product Class 24: Azoxyarenes (Di- and Monoaryldiazene Oxides) K. Rück-Braun and B. Priewisch	
31.24	Product Class 24: Azoxyarenes (Di- and Monoaryldiazene Oxides)	1401
31.24.1	Product Subclass 1: Symmetrically Substituted Diaryldiazene Oxides ...	1401
31.24.1.1	Synthesis of Product Subclass 1	1402
31.24.1.1.1	Method 1: Reduction of Nitroarenes	1402
31.24.1.1.1.1	Variation 1: Reduction with Glucose	1403
31.24.1.1.1.2	Variation 2: Reduction with Zinc/Aluminum Trichloride	1403
31.24.1.1.1.3	Variation 3: Reduction with Bismuth	1404
31.24.1.1.1.4	Variation 4: Catalytic Hydrogenation	1405
31.24.1.1.1.5	Variation 5: Electrochemical Reduction	1406
31.24.1.1.2	Method 2: Condensation of Nitrosoarenes with <i>N</i> -Arylhydroxylamines	1407
31.24.1.1.3	Method 3: Oxidation of Anilines	1408
31.24.1.1.3.1	Variation 1: Oxidation with Peroxy Acids	1408
31.24.1.1.3.2	Variation 2: Catalytic Oxidation with Hydrogen Peroxide	1408
31.24.1.1.4	Method 4: Oxidation of Diaryldiazenes with Peroxy Acids	1409
31.24.2	Product Subclass 2: Unsymmetrically Substituted Diaryldiazene Oxides	1410
31.24.2.1	Synthesis of Product Subclass 2	1411
31.24.2.1.1	Method 1: Oxidation of Diaryldiazenes	1411
31.24.2.1.2	Method 2: Reaction of Nitroarenes with (Arylimino)dimagnesium Reagents	1412
31.24.2.1.3	Method 3: Reaction of 1-Aryl-2-(tosyloxy)diazene 1-Oxides and 1-Aryl-2-fluorodiazene 1-Oxides with Aryl Grignard Reagents	1413
31.24.2.1.4	Method 4: Oxidation of Indazole Oxides	1413
31.24.2.1.5	Method 5: Electrophilic Substitution of Diaryldiazene Oxides	1414
31.24.3	Product Subclass 3: Monoaryldiazene Oxides	1416
31.24.3.1	Synthesis of Product Subclass 3	1416
31.24.3.1.1	Method 1: Condensation of Nitrosoarenes with <i>N,N</i> -Dihaloalkylamines	1416
31.24.3.1.2	Method 2: Reaction of 1-Aryl-2-(tosyloxy)diazene 1-Oxides and 1-Aryl- 2-fluorodiazene 1-Oxides with Alkyl Grignard Reagents	1417
31.24.3.1.3	Method 3: Oxidation of Alkyl(aryl)diazenes	1417
31.24.3.1.4	Method 4: Oxidation of Hydrazones	1418

31.24.3.1.5	Method 5:	Condensation of Nitrosoarenes with <i>N</i> -Alkylhydroxylamines	1419
31.24.3.1.6	Method 6:	Functional-Group Transformations	1419
31.25	Product Class 25: Azoarenes		
	K. Rück-Braun, S. Dietrich, S. Kempa, and B. Prieswisch		
31.25	Product Class 25: Azoarenes		1425
31.25.1	Product Subclass 1: Diaryldiazenes		1425
31.25.1.1	Synthesis of Product Subclass 1		1426
31.25.1.1.1	Coupling of Arenediazonium Salts		1426
31.25.1.1.1.1	Method 1:	Coupling with Phenols	1427
31.25.1.1.1.2	Method 2:	Coupling with Aryl Ethers	1434
31.25.1.1.1.3	Method 3:	Coupling with Arylamines	1438
31.25.1.1.1.3.1	Variation 1:	Coupling of (Arylamino)methanesulfonic Acids	1443
31.25.1.1.1.3.2	Variation 2:	Rearrangement of Triazenes	1445
31.25.1.1.1.4	Method 4:	Coupling with Arylhydrazine Derivatives	1446
31.25.1.1.1.5	Method 5:	Coupling with Nonactivated Arenes and Hetarenes	1447
31.25.1.1.1.6	Method 6:	Coupling of Diazonium Salts with Elimination of Nitrogen	1451
31.25.1.1.1.7	Method 7:	Synthesis of Polyazo Compounds	1452
31.25.1.1.1.7.1	Variation 1:	Coupling with Azo Compounds	1455
31.25.1.1.2	Condensation Reactions		1457
31.25.1.1.2.1	Method 1:	Condensation of Nitrosoarenes with Arylamines in Acetic Acid	1457
31.25.1.1.2.2	Method 2:	Condensation of Nitrosoarenes with Arylamines in the Presence of a Base	1459
31.25.1.1.2.3	Method 3:	Condensation of Nitroarenes with Arylamines in Aqueous Sodium Hydroxide	1461
31.25.1.1.2.3.1	Variation 1:	Condensation of Nitroarenes with Arylamines in the Presence of Powdered Sodium Hydroxide	1462
31.25.1.1.2.4	Method 4:	Condensation of Nitroarenes with Acetylated Arylamines	1463
31.25.1.1.2.5	Method 5:	Condensation of Arylhydrazines with Quinones	1464
31.25.1.1.2.5.1	Variation 1:	Condensation with Cyclohexadienones	1466
31.25.1.1.2.5.2	Variation 2:	Condensation with Quinone Diacetals	1468
31.25.1.1.3	Reduction of Nitroarenes		1468
31.25.1.1.3.1	Method 1:	Reduction with Zinc	1469
31.25.1.1.3.2	Method 2:	Reduction with Glucose	1470
31.25.1.1.3.3	Method 3:	Catalytic Hydrogenation	1471
31.25.1.1.3.3.1	Variation 1:	Catalytic Transfer Hydrogenation	1471
31.25.1.1.3.4	Method 4:	Reduction with Lithium Aluminum Hydride	1472
31.25.1.1.3.4.1	Variation 1:	Reduction with Sodium Bis(2-methoxyethoxy)aluminum Hydride	1474
31.25.1.1.3.4.2	Variation 2:	Reduction with Sodium Borohydride	1474
31.25.1.1.3.5	Method 5:	Electrochemical Reduction	1475
31.25.1.1.4	Reduction of Diaryldiazene Oxides		1476
31.25.1.1.4.1	Method 1:	Reduction of Diaryldiazene Oxides	1476

31.25.1.1.5	Oxidation of Arylamines	1478
31.25.1.1.5.1	Method 1: Oxidation Using Hypohalites	1479
31.25.1.1.5.2	Method 2: Oxidation Using Manganese(IV) Oxide	1480
31.25.1.1.5.2.1	Variation 1: Using Manganates or Permanganates	1481
31.25.1.1.5.3	Method 3: Oxidation Using Oxygen	1482
31.25.1.1.5.4	Method 4: Oxidation Using Sodium Perborate in Acetic Acid	1484
31.25.1.1.5.5	Method 5: Oxidation Using Potassium Hexacyanoferrate(III)	1485
31.25.1.1.6	Oxidation of 1,2-Diarylhydrazines	1486
31.25.1.1.6.1	Method 1: Oxidation Using Hypohalites	1486
31.25.1.1.6.2	Method 2: Oxidation Using Oxygen	1487
31.25.1.1.6.3	Method 3: Oxidation Using Manganese(IV) Oxide	1489
31.25.1.1.7	Oxidation of <i>tert</i> -Butyl 1,2-Diarylhydrazinecarboxylates	1490
31.25.1.1.7.1	Method 1: Oxidation Using <i>N</i> -Bromosuccinimide	1490
31.25.1.1.7.2	Method 2: Oxidation Using Copper(I) Iodide in the Presence of Cesium Carbonate	1490
31.25.1.1.8	Transformations with Retention of the Functional Group	1493
31.25.1.1.8.1	Method 1: Electrophilic Aromatic Substitution of Hydrogen	1493
31.25.1.1.8.2	Method 2: C—H Bond Activation by Transition Metals	1494
31.25.1.1.8.3	Method 3: Nucleophilic Aromatic Substitution Reactions	1495
31.25.1.1.8.3.1	Variation 1: Substitution of Halogens	1496
31.25.1.1.8.3.2	Variation 2: Substitution of Amino and Hydroxy Groups	1497
31.25.1.1.8.3.3	Variation 3: Displacement of Hydroxy Groups by Phosphoryl Chloride	1497
31.25.1.1.8.4	Method 4: Palladium-Catalyzed Cross-Coupling Reactions	1499
31.25.1.1.8.5	Method 5: Transformation of Functional Groups Attached to the Aromatic Ring	1502
31.25.2	Product Subclass 2: 1-Alkyl-2-aryldiazenes	1502
31.25.2.1	Synthesis of Product Subclass 2	1502
31.25.2.1.1	Formation of the N=N Bond	1503
31.25.2.1.1.1	Method 1: Condensation of Nitrosobenzene with Aliphatic Amines	1503
31.25.2.1.2	Synthesis from Compounds Containing a N—N Bond	1505
31.25.2.1.2.1	Method 1: Condensation of Arenediazonium Salts with CH-Acidic Compounds	1505
31.25.2.1.2.2	Method 2: Reaction of Arenediazonium Salts with Organometallic Compounds	1509
31.25.2.1.2.3	Method 3: Reductive Alkylation of Arenediazonium Salts	1510
31.25.2.1.2.4	Method 4: Oxidation of Arylhydrazones	1514
31.25.2.1.2.5	Method 5: Ene-Type Reactions of Arylhydrazones	1518
31.25.2.1.2.6	Method 6: Allylation of Arylhydrazones	1520
31.25.2.1.2.7	Method 7: Oxidation of 1-Alkyl-2-arylhydrazines	1520
31.25.2.1.2.8	Method 8: Rearrangement of 1-Alkyl-3-arylureas	1523
31.25.2.1.2.9	Method 9: Reduction of 1-Alkyl-2-aryldiazene Oxides	1524

31.26	Product Class 26: (Arylimino)phosphines and (Arylimino)phosphoranes M. Alajarín, C. López-Leonardo, and J. Berná	
31.26	Product Class 26: (Arylimino)phosphines and (Arylimino)phosphoranes	1539
31.26.1	Product Subclass 1: (Arylimino)phosphines	1539
31.26.1.1	Synthesis of Product Subclass 1	1539
31.26.1.1.1	Method 1: Dehydrohalogenation of Compounds Bearing N—P—X Units	1539
31.26.1.1.1.1	Variation 1: One-Pot Reaction of Arylamines with Di- or Trihalophosphines	1540
31.26.1.1.2	Method 2: β -Elimination of Halosilanes	1541
31.26.1.1.3	Method 3: β -Elimination of Secondary Amines	1542
31.26.1.1.4	Method 4: Halogen Substitution in Halo(imino)phosphines	1543
31.26.2	Product Subclass 2: (Arylimino)phosphoranes	1544
31.26.2.1	Synthesis of Product Subclass 2	1545
31.26.2.1.1	Method 1: Imination of Tertiary Phosphines with Azides	1545
31.26.2.1.2	Method 2: Reaction of Arylamines with Dihalophosphoranes	1547
31.26.2.1.3	Method 3: Reaction of Arylamines with Phosphino Dialkyl Azodicarboxylate Betaines	1549
31.26.2.1.4	Method 4: Reaction of Activated Aryl Fluorides with (Silylimino)phosphoranes	1549
31.26.2.1.5	Method 5: P-Alkylation of <i>N</i> -Phosphinoarylamines	1550
31.26.2.2	Applications of Product Subclass 2 in Organic Synthesis	1551
31.26.2.2.1	Method 1: Reactions of (Arylimino)phosphoranes with Carbonyl Compounds (The Aza-Wittig Reaction)	1551
31.27	Product Class 27: Arylamine <i>N</i>-Oxides and Arylaminoxyl Radicals A. Schmidt	
31.27	Product Class 27: Arylamine <i>N</i>-Oxides and Arylaminoxyl Radicals	1555
31.27.1	Product Subclass 1: Arylamine <i>N</i>-Oxides	1555
31.27.1.1	Synthesis of Product Subclass 1	1555
31.27.1.1.1	Method 1: Oxidation of Tertiary Amines	1555
31.27.1.1.1.1	Variation 1: With Oxygen	1555
31.27.1.1.1.2	Variation 2: With Hydrogen Peroxide	1555
31.27.1.1.1.3	Variation 3: With Peroxycarboxylic Acids	1556
31.27.2	Product Subclass 2: Arylaminoxyl Radicals	1557
31.27.2.1	Synthesis of Product Subclass 2	1559
31.27.2.1.1	Method 1: Oxidation of Hydroxylamines	1559
31.27.2.1.1.1	Variation 1: With Silver(I) Oxide	1559
31.27.2.1.1.2	Variation 2: With Lead(IV) Oxide	1560
31.27.2.1.1.3	Variation 3: With Sodium Periodate	1562
31.27.2.1.1.4	Variation 4: With Air	1563
31.27.2.1.2	Method 2: Reaction of Nitrosoarenes with Tricarbonyl- (η^5 -cyclohexadienyl)iron(II)	1563

31.28 Product Class 28: Arylamines

U. Scholz and B. Schlummer

31.28	Product Class 28: Arylamines	1565
31.28.1	Synthesis of Product Class 28	1565
31.28.1.1	Method 1: Direct Introduction of Nitrogen Using Bases	1565
31.28.1.2	Method 2: Direct Introduction of Nitrogen Using Acids	1567
31.28.1.2.1	Variation 1: Using Aluminum Trichloride and Sodium Azide	1567
31.28.1.2.2	Variation 2: Using Aluminum Trichloride and Trichloroamine	1568
31.28.1.2.3	Variation 3: Using Aluminum Trichloride and Dichloroamine	1569
31.28.1.2.4	Variation 4: Using Dialkylchloroamines and Metal Salts	1569
31.28.1.2.5	Variation 5: Using Trifluoromethanesulfonic Acid and Azides	1570
31.28.1.2.6	Variation 6: Using Hydroxylamine Derivatives and Acids	1571
31.28.1.3	Method 3: Catalytic Direct Amination	1572
31.28.1.4	Method 4: Direct Amination of Activated Aromatic Systems	1572
31.28.1.4.1	Variation 1: Using Ammonia–Potassium Amide and Potassium Permanganate	1572
31.28.1.4.2	Variation 2: Using Cobalt(II) Chloride, Oxygen, and Hydrogen Sulfide	1573
31.28.1.4.3	Variation 3: Using Hydroxylamine	1574
31.28.1.5	Method 5: Substitution of Fluoroarenes	1574
31.28.1.5.1	Variation 1: Using Ammonia	1574
31.28.1.5.2	Variation 2: Using Primary or Secondary Amines	1576
31.28.1.5.3	Variation 3: Using Tertiary Amines	1577
31.28.1.5.4	Variation 4: Using Amides, Metal Amides, or Imides	1578
31.28.1.5.5	Variation 5: Using Ammonium Salts	1579
31.28.1.6	Method 6: Substitution of Chloroarenes	1579
31.28.1.6.1	Variation 1: Using Ammonia	1579
31.28.1.6.2	Variation 2: Using Primary or Secondary Amines	1581
31.28.1.6.3	Variation 3: Using Tertiary Amines	1587
31.28.1.6.4	Variation 4: Using Amides, Metal Amides, or Imides	1588
31.28.1.6.5	Variation 5: Using Ammonium Salts	1589
31.28.1.7	Method 7: Substitution of Bromoarenes	1589
31.28.1.7.1	Variation 1: Using Ammonia	1589
31.28.1.7.2	Variation 2: Using Primary or Secondary Amines	1591
31.28.1.7.3	Variation 3: Using Amides, Metal Amides, or Imides	1595
31.28.1.8	Method 8: Substitution of Iodoarenes	1597
31.28.1.8.1	Variation 1: Using Ammonia	1597
31.28.1.8.2	Variation 2: Using Primary or Secondary Amines	1598
31.28.1.8.3	Variation 3: Using Amides, Metal Amides, or Imides	1601
31.28.1.9	Method 9: Substitution of Phenols	1601
31.28.1.9.1	Variation 1: Using Ammonia	1601
31.28.1.9.2	Variation 2: Using Primary or Secondary Amines	1603
31.28.1.9.3	Variation 3: Using Amides, Metal Amides, or Imides	1605
31.28.1.9.4	Variation 4: Using Ammonium Salts	1605
31.28.1.10	Method 10: Substitution of Aryl Ethers and Esters	1606
31.28.1.10.1	Variation 1: Using Ammonia	1606
31.28.1.10.2	Variation 2: Using Primary or Secondary Amines	1606

31.28.1.10.3	Variation 3:	Using Amides, Metal Amides, or Imides	1609
31.28.1.10.4	Variation 4:	Using Ammonium Salts	1610
31.28.1.11	Method 11:	Substitution of Aryl Sulfides and Sulfonates	1611
31.28.1.11.1	Variation 1:	Using Primary or Secondary Amines	1611
31.28.1.11.2	Variation 2:	Using Amides, Metal Amides, or Imides	1611
31.28.1.12	Method 12:	Substitution of Nitroarenes	1611
31.28.1.12.1	Variation 1:	Using Ammonia	1611
31.28.1.12.2	Variation 2:	Using Primary or Secondary Amines	1612
31.28.1.13	Method 13:	Substitution of Other Aryl Derivatives	1613
31.28.1.13.1	Variation 1:	Substitution of Arylplumbanes	1613
31.28.1.13.2	Variation 2:	Substitution of Arylbismuthanes	1613
31.28.1.13.3	Variation 3:	Substitution of Arylsiloxanes	1614
31.28.1.13.4	Variation 4:	Substitution of Arylstannanes	1615
31.28.1.13.5	Variation 5:	Substitution of Arylboronic Acids	1615
31.28.1.13.6	Variation 6:	Substitution of Arylmagnesium Compounds	1616
31.28.1.13.7	Variation 7:	Substitution of Arenecarbonitriles	1616
31.28.1.13.8	Variation 8:	Substitution of Arylzincates	1617
31.28.1.13.9	Variation 9:	Substitution of Arylantimonates	1617
31.28.1.14	Method 14:	Reduction of Nitroarenes	1618
31.28.1.14.1	Variation 1:	Using Transfer Hydrogenation	1618
31.28.1.14.2	Variation 2:	Using Direct Hydrogenation	1619
31.28.1.14.3	Variation 3:	Using Iron	1621
31.28.1.14.4	Variation 4:	Using Sulfur	1622
31.28.1.14.5	Variation 5:	Using Tin	1623
31.28.1.14.6	Variation 6:	Using Hydrazine	1624
31.28.1.14.7	Variation 7:	Using Complex Metal Hydrides	1625
31.28.1.14.8	Variation 8:	Using Zinc	1625
31.28.1.14.9	Variation 9:	Using Aluminum	1626
31.28.1.14.10	Variation 10:	Using Alkali Metals	1627
31.28.1.14.11	Variation 11:	Using Electrochemical Methods	1627
31.28.1.15	Method 15:	Reduction of Nitrosoarenes	1628
31.28.1.16	Method 16:	Reduction of Arylamine <i>N</i> -Oxides	1629
31.28.1.17	Method 17:	Reduction of Azo Compounds	1630
31.28.1.18	Method 18:	Reduction of Azides	1631
31.28.1.19	Method 19:	Reduction of Isocyanates	1631
31.28.1.20	Method 20:	Reduction of Imines	1632
31.28.1.21	Method 21:	Reduction of <i>N</i> -Nitrosoanilines	1634
31.28.1.22	Method 22:	Reduction of Azoxy Compounds	1635
31.28.1.23	Method 23:	Reduction of Hydrazines	1636
31.28.1.24	Method 24:	Reduction of Aminals	1637
31.28.1.25	Method 25:	Reduction of Amides	1637
31.28.1.26	Method 26:	Reduction of Carbamates	1638
31.28.1.27	Method 27:	Reduction of Imidoyl Chlorides	1638
31.28.1.28	Method 28:	Partial Reduction of Quinolines	1639
31.28.1.29	Method 29:	Alkylation of Benzo-1,4-quinone Derivatives	1640
31.28.1.29.1	Variation 1:	Aromatic Alkylation of Benzo-1,4-quinone Diimines	1640
31.28.1.29.2	Variation 2:	Aromatization of Benzo-1,4-quinone Oximes	1641
31.28.1.29.3	Variation 3:	Aromatization of Benzo-1,2-quinones	1641

31.28.1.30	Method 30:	Synthesis from Cyclic Oximes	1642
31.28.1.31	Method 31:	Synthesis from Cyclohexanones	1642
31.28.1.32	Method 32:	Cyclization of Nitriles	1644
31.28.1.33	Method 33:	Synthesis by Rearrangement	1644
31.28.1.33.1	Variation 1:	Replacement of an Aromatic C—H Bond by a C—S Bond	1644
31.28.1.33.2	Variation 2:	Replacement of an Aromatic C—H Bond by a C—N Bond	1645
31.28.1.33.3	Variation 3:	Replacement of an Aromatic C—H Bond by a C—C Bond	1646
31.28.1.33.4	Variation 4:	Replacement of an Aromatic C—C Bond by a C—N Bond	1649
31.28.1.33.5	Variation 5:	Replacement of an Aromatic C—O Bond by a C—N Bond	1652
31.28.1.33.6	Variation 6:	Replacement of an Aromatic C—S Bond by a C—N Bond	1653
31.28.1.33.7	Variation 7:	Replacement of an Aromatic C—H Bond by a C—O Bond	1654
31.28.1.34	Method 34:	Synthesis by Transamination	1654
31.28.1.34.1	Variation 1:	Using Primary or Secondary Amines	1654
31.28.1.34.2	Variation 2:	Using Ammonium Salts	1657
31.28.1.35	Method 35:	Reaction of Arylamines with Alkyl Halides or Pseudohalides	1657
31.28.1.36	Method 36:	Reaction of Arylsilanamines with Alkyl Halides	1658
31.28.1.37	Method 37:	Reaction of Arylamines with Aliphatic Alcohols	1659
31.28.1.38	Method 38:	Reaction of Arylamines with Aldehydes or Ketones	1659
31.28.1.39	Method 39:	Reaction of Arylamines with Esters	1660
31.28.1.39.1	Variation 1:	Using Reactive Esters	1660
31.28.1.39.2	Variation 2:	Using Carboxylic Esters	1661
31.28.1.40	Method 40:	Reaction of Arylamines with Alkenes	1662
31.28.1.40.1	Variation 1:	Hydroamination Reactions	1662
31.28.1.40.2	Variation 2:	Michael Addition Reactions	1663
31.28.1.41	Method 41:	Reaction of Arylamines with Alkynes	1665
31.28.1.42	Method 42:	Reaction of Arylamines with Epoxides, Cyclic Ethers, or Aziridines	1666
31.28.1.43	Method 43:	Reaction of Arylamines with Lactones	1667
31.28.1.44	Method 44:	Dealkylation Reactions	1667

31.29 Product Class 29: Arylammonium Salts

B. Schlummer and U. Scholz

31.29	Product Class 29: Arylammonium Salts	1679
31.29.1	Synthesis of Product Class 29	1680
31.29.1.1	Method 1: Alkylation or Arylation of Tertiary Amines	1680
31.29.1.1.1	Variation 1: Using Esters of Strong Acids	1680
31.29.1.1.2	Variation 2: Using Organic Halides	1681
31.29.1.1.3	Variation 3: Using Alkenes or Alkynes	1683
31.29.1.1.4	Variation 4: Using Carbonyl Compounds	1683
31.29.1.1.5	Variation 5: Using Onium Salts	1683
31.29.1.1.6	Variation 6: Using Epoxides	1684
31.29.1.1.7	Variation 7: Using Lactones	1684
31.29.1.2	Method 2: Alkylation or Arylation of Primary and Secondary Amines	1684
31.29.1.3	Method 3: Acylation of Tertiary Amines	1685
31.29.1.4	Method 4: Quaternary Ammonium Salts from Other Quaternary Ammonium Compounds	1686

31.29.1.4.1	Variation 1:	Anion Exchange	1686
31.29.1.4.2	Variation 2:	Quaternary Ammonium Hydroxide Formation	1686
31.29.1.4.3	Variation 3:	Halogen Addition	1688
31.29.1.4.4	Variation 4:	Formation of Betaines	1688
31.29.2	Applications of Product Class 29 in Organic Synthesis		1688
31.29.2.1	Method 1:	Formation of Tertiary Amines	1689
31.29.2.2	Method 2:	Quaternary Ammonium Compounds as Alkylating Agents	1689
31.29.2.3	Method 3:	Rearrangements	1690
31.29.2.4	Method 4:	Hofmann Elimination	1691
31.29.2.5	Method 5:	Phase-Transfer Catalysts	1692
31.30	Product Class 30: <i>N</i>-Silylarylamines		
	J. L. Chiara		
31.30	Product Class 30: <i>N</i>-Silylarylamines		1697
31.30.1	Synthesis of Product Class 30		1697
31.30.1.1	Method 1:	Reaction of Organosilanes with Arylamines	1697
31.30.1.1.1	Variation 1:	Using Cesium Fluoride	1697
31.30.1.1.2	Variation 2:	Using Transition-Metal Catalysts	1697
31.30.1.2	Method 2:	Reaction of Halosilanes with Arylamines	1698
31.30.1.2.1	Variation 1:	Reaction of Chloro[2-[chloro(dimethyl)silyl]ethyl]- dimethylsilane with Primary <i>N</i> -Arylamines	1700
31.30.1.3	Method 3:	Synthesis Using Silyl Trifluoromethanesulfonates	1700
31.30.1.3.1	Variation 1:	Reaction with Arylamines	1700
31.30.1.3.2	Variation 2:	Reaction with <i>N</i> -Arylimines	1701
31.30.1.4	Method 4:	Synthesis from Silyl Trichloroacetates and Arylamines	1701
31.30.1.5	Method 5:	Synthesis from <i>N,N</i> -Dialkylaminosilanes and Arylamines	1701
31.30.1.6	Method 6:	Synthesis from Hexamethyldisilazane and Arylamines	1702
31.30.1.7	Method 7:	Synthesis from Haloarenes and Metal Hexamethyldisilazanides	1702
31.30.1.8	Method 8:	Hydrosilylation of Imines	1703
31.30.1.9	Method 9:	Reductive Silylation of Trifluoromethylimines	1704
31.30.1.10	Method 10:	Reductive Silylation of Azo Compounds	1705
31.30.1.11	Method 11:	Reductive Silylation of Nitroarenes	1706
31.30.1.11.1	Variation 1:	Reduction with Triethylsilane	1706
31.30.1.11.2	Variation 2:	Reduction with Chromium(II)/Manganese(0)	1707
31.30.1.12	Method 12:	Synthesis of Stable <i>N</i> -Arylsilanamines	1707
31.30.1.13	Method 13:	Synthesis of Lithium <i>N</i> -Arylsilaamidides	1707
31.30.1.14	Method 14:	Synthesis of <i>N,N'</i> -Neopentyl-1,2-phenylenediaminosilylene	1708
31.30.1.15	Method 15:	Aza-Brook Rearrangement of (α -Silylallyl)amines to <i>N</i> -Silylenamines	1709

31.31 Product Class 31: *N*-Borylarylamines

J. L. Chiara

31.31	Product Class 31: <i>N</i>-Borylarylamines	1711
31.31.1	Synthesis of Product Class 31	1712
31.31.1.1	Method 1: Synthesis from Arylamines	1712
31.31.1.1.1	Variation 1: By Reaction with Boranes	1713
31.31.1.1.2	Variation 2: By Reaction with Trialkylboranes	1715
31.31.1.1.3	Variation 3: By Reaction with Haloboranes	1715
31.31.1.1.4	Variation 4: By Reaction with Organooxyboranes	1717
31.31.1.1.5	Variation 5: By Reaction with Sulfanylboranes	1718
31.31.1.1.6	Variation 6: By Reaction with Aminoboranes	1719
31.31.1.2	Method 2: Redistribution and Exchange Reactions	1719
31.31.1.3	Method 3: Reductive Alkylation of Azides	1719
31.31.1.4	Method 4: Synthesis from Imines	1719
31.31.1.4.1	Variation 1: By Hydroboration	1720
31.31.1.4.2	Variation 2: By Diboration	1721
31.31.1.5	Method 5: Borylation of Organometallic Reagents	1721

31.32 Product Class 32: *N*-Haloarylamines

J. L. Chiara

31.32	Product Class 32: <i>N</i>-Haloarylamines	1725
31.32.1	Synthesis of Product Class 32	1727
31.32.1.1	Method 1: Synthesis from Arylamines	1727
31.32.1.1.1	Variation 1: By Reaction with Halogens	1727
31.32.1.1.2	Variation 2: By Reaction with Inorganic or Organic Hypochlorites	1729
31.32.1.1.3	Variation 3: By Reaction with Dichlorine Monoxide	1731
31.32.1.1.4	Variation 4: By Reaction with <i>N</i> -Halosuccinimides	1731
31.32.1.1.5	Variation 5: By Reaction with Sulfuryl Chloride	1732
31.32.1.2	Method 2: Synthesis from <i>N</i> -Haloarylamines by Halogen Exchange	1732
31.32.1.3	Method 3: Synthesis from Imines	1733
31.32.1.3.1	Variation 1: By Reaction with Halogens	1733
31.32.1.3.2	Variation 2: By Reaction with Hypofluorites	1733
31.32.1.3.3	Variation 3: By Reaction with Cyanogen Bromide	1734
31.32.1.4	Method 4: Synthesis from Orthoamides	1735

31.33 Product Class 33: *N*-Arylhydroxylamines

A. Schmidt

31.33	Product Class 33: <i>N</i>-Arylhydroxylamines	1739
31.33.1	Synthesis of Product Class 33	1739
31.33.1.1	Method 1: Substitution of Hydrogen at the the N—H Group of Hydroxylamine and <i>N</i> -Alkylhydroxylamines by Aryl Groups	1739
31.33.1.1.1	Variation 1: From Aryl and Hetaryl Halides	1739

31.33.1.1.2	Variation 2:	From Hydroxy- or Alkoxy-Substituted Arenes	1744
31.33.1.1.3	Variation 3:	From a Nitrobenzene	1744
31.33.1.1.4	Variation 4:	From an Arenesulfonate	1745
31.33.1.1.5	Variation 5:	From 4-(Nitroamino)pyrimidines	1745
31.33.1.2	Method 2:	Oxidation of a Dihydroindole To Give an <i>N</i> -Hydroxyindole	1745
31.33.1.3	Method 3:	Reaction of an Aniline with <i>N</i> -(Trifluoroacetoxy)succinimide To Give an <i>O</i> -Acyl- <i>N</i> -phenylhydroxylamine	1746
31.33.1.4	Method 4:	Substitution Reaction between <i>N</i> -Benzylhydroxylamine and Hexafluorobenzene To Give <i>N</i> -(Pentafluorophenyl)hydroxyl- amine	1746
31.33.1.5	Method 5:	Reduction of Nitro Compounds	1747
31.33.1.5.1	Variation 1:	By Catalytic Reduction	1747
31.33.1.5.2	Variation 2:	With Hydrazine	1748
31.33.1.5.3	Variation 3:	With Hypophosphites	1750
31.33.1.5.4	Variation 4:	With Zinc Dust	1750
31.33.1.5.5	Variation 5:	With Tin(II) Chloride	1752
31.33.1.5.6	Variation 6:	With Titanium(III) Chloride	1753
31.33.1.5.7	Variation 7:	With Ammonium Sulfide	1754
31.33.1.5.8	Variation 8:	By Addition of Grignard Reagents	1754
31.33.1.5.9	Variation 9:	Indium-Mediated Reductive Acylations and Allylations	1755
31.33.1.5.10	Variation 10:	By Borohydride	1756
31.33.1.5.11	Variation 11:	Electrochemical Reduction	1756
31.33.1.5.12	Variation 12:	With Baker's Yeast	1756
31.33.1.6	Method 6:	Synthesis from Nitroso Compounds	1756
31.33.1.6.1	Variation 1:	Reaction with Grignard and Organolithium Reagents	1756
31.33.1.6.2	Variation 2:	Addition of Lithium or Tin Enolates to Nitrosobenzene (Nitroso Aldol Synthesis)	1757
31.33.1.6.3	Variation 3:	<i>O</i> -Selective Nucleophilic Addition of Silyl Enol Ethers Promoted by Lewis Acids	1759
31.33.1.6.4	Variation 4:	By α -Oxyamination of Aldehydes and Ketones with Proline and Other Asymmetric Organocatalysts	1760
31.33.1.6.5	Variation 5:	By α -Oxyamination of Enamines	1763
31.33.1.6.6	Variation 6:	By Allylboration of Nitrosobenzene	1764
31.33.1.6.7	Variation 7:	Reaction between Nitrosobenzene and 2- and 3-Vinylindoles	1764
31.33.1.7	Method 7:	Nucleophilic Addition to Nitrones	1765
31.33.1.8	Method 8:	Rearrangement Reactions	1766
31.33.1.9	Method 9:	Ring Cleavage of Isoxazoles	1768
31.33.1.10	Method 10:	<i>N</i> -Hetarylhydroxylamines from 4-Hydroxythiosemicarbazides	1768

31.34 Product Class 34: Arylhydrazines

M. Begtrup and L. K. Rasmussen

31.34	Product Class 34: Arylhydrazines	1773
31.34.1	Product Subclass 1: Unsubstituted Arylhydrazines	1774
31.34.1.1	Synthesis of Product Subclass 1	1774
31.34.1.1.1	Method 1: Reduction of Arenediazonium Salts Derived from Arylamines	1774

31.34.1.1.1.1	Variation 1:	Using Sodium Sulfite or Sodium Hydrogen Sulfite	1774
31.34.1.1.1.2	Variation 2:	Using Tin(II) Chloride	1775
31.34.1.1.2	Method 2:	Nucleophilic Aromatic Substitution	1776
31.34.1.1.3	Method 3:	Transition-Metal-Catalyzed N-Arylation of Hydrazine Derivatives	1777
31.34.1.1.3.1	Variation 1:	Palladium-Catalyzed N-Arylation of Benzophenone Hydrazone Followed by Hydrolysis	1777
31.34.1.1.3.2	Variation 2:	Copper-Catalyzed N-Arylation of <i>tert</i> -Butoxycarbonylhydrazine	1778
31.34.1.1.3.3	Variation 3:	Copper-Assisted N-Arylation of <i>tert</i> -Butoxycarbonylhydrazine with a Triarylbi-muthine or a Triarylbi-muth Diacetate	1779
31.34.1.1.4	Method 4:	Electrophilic Hydrazination of Arenes	1780
31.34.1.1.5	Method 5:	Electrophilic Hydrazination of Metalated Arenes	1781
31.34.1.1.6	Method 6:	Electrophilic N-Amination of Anilines	1782
31.34.1.1.7	Methods 7:	Miscellaneous Methods	1782
31.34.2	Product Subclass 2: 1-Alkyl-1-arylhydrazines		1783
31.34.2.1	Synthesis of Product Subclass 2		1783
31.34.2.1.1	Method 1:	Nucleophilic Aromatic Substitution	1783
31.34.2.1.2	Method 2:	Alkylation of Arylhydrazines	1783
31.34.2.1.3	Method 3:	Alkylation of Sodium Hydrazides	1784
31.34.2.1.4	Method 4:	Reduction of <i>N</i> -Nitrosoanilines	1784
31.34.2.1.5	Methods 5:	Miscellaneous Methods	1785
31.34.3	Product Subclass 3: 1-Alkyl-2-arylhydrazines		1785
31.34.3.1	Synthesis of Product Subclass 3		1785
31.34.3.1.1	Method 1:	Alkylation of Arylhydrazines	1785
31.34.3.1.2	Method 2:	Alkylation and Arylation of Protected Hydrazine Derivatives	1786
31.34.3.1.3	Method 3:	Reduction of Arylhydrazides and Arylhydrazones	1787
31.34.4	Product Subclass 4: 1,2-Dialkyl-1-arylhydrazines		1787
31.34.4.1	Synthesis of Product Subclass 4		1787
31.34.4.1.1	Method 1:	Alkylation of (2-Phenylhydrazino)triphenylphosphorane	1788
31.34.4.1.2	Method 2:	Reduction of 2-Alkyl-2-arylhydrazones	1788
31.34.4.1.2.1	Variation 1:	Using Lithium	1789
31.34.4.1.2.2	Variation 2:	Using Lithium Aluminum Hydride	1789
31.34.4.1.3	Method 3:	Reduction of 2-Acyl-2-arylhydrazones	1789
31.34.5	Product Subclass 5: 1,1-Dialkyl-2-arylhydrazines		1790
31.34.5.1	Synthesis of Product Subclass 5		1790
31.34.5.1.1	Method 1:	N-Arylation	1790
31.34.5.1.1.1	Variation 1:	Of 1,1-Disubstituted Hydrazines Using an Activated Arene	1790
31.34.5.1.1.2	Variation 2:	Of 1,1-Dialkylhydrazines Using Bromoarenes	1791
31.34.5.1.1.3	Variation 3:	Of 1,1-Dialkylhydrazines with Halides or Trifluoromethanesulfonates	1792
31.34.5.1.2	Method 2:	Electrophilic Amination of Secondary Amines with <i>N</i> -Aryl- <i>O</i> -(diphenylphosphoryl)hydroxylamine	1792
31.34.5.1.3	Methods 3:	Miscellaneous Methods	1793

31.34.6	Product Subclass 6: 1,1,2-Trialkyl-2-arylhydrazines	1793
31.34.6.1	Synthesis of Product Subclass 6	1793
31.34.6.1.1	Method 1: Alkylation of 1,1-Dialkyl-2-arylhydrazines	1793
31.34.7	Product Subclass 7: 1,1-Diarylhydrazines	1794
31.34.7.1	Synthesis of Product Subclass 7	1794
31.34.7.1.1	Method 1: Reduction of <i>N</i> -Nitroso Compounds	1794
31.34.7.1.2	Method 2: Rearrangement Reactions	1795
31.34.7.1.3	Methods 3: Miscellaneous Methods	1796
31.34.8	Product Subclass 8: 1-Alkyl-2,2-diarylhydrazines	1796
31.34.8.1	Synthesis of Product Subclass 8	1796
31.34.8.1.1	Method 1: Copper-Catalyzed Ethylation of 1,1-Diarylhydrazines Using Diethylzinc(II)	1796
31.34.8.1.2	Method 2: Alkylation of 1,1-Diarylhydrazines Using Lithium Alkylcyanocuprates	1796
31.34.9	Product Subclass 9: 1,1-Dialkyl-2,2-diarylhydrazines	1797
31.34.9.1	Synthesis of Product Subclass 9	1797
31.34.10	Product Subclass 10: 1,2-Diarylhydrazines	1797
31.34.10.1	Synthesis of Product Subclass 10	1797
31.34.10.1.1	Method 1: Reduction of Nitroarenes	1797
31.34.10.1.1.1	Variation 1: Using Zinc	1798
31.34.10.1.1.2	Variation 2: Using Magnesium	1798
31.34.10.1.1.3	Variation 3: Using Aluminum	1798
31.34.10.1.2	Method 2: Reduction of Azoxybenzenes	1799
31.34.10.1.2.1	Variation 1: Using an Aromatic Secondary Alcohol and Sodium Hydroxide	1799
31.34.10.1.2.2	Variation 2: Using Sodium Dithionite and 1,1'-Dioctyl-4,4'-bipyridinium Dichloride (Dioctylviologen) as an Electron-Transfer Catalyst	1800
31.34.10.1.2.3	Variation 3: Using Sodium Borohydride and Iodine in Tetrahydrofuran	1800
31.34.10.1.2.4	Variation 4: Electrochemical Reduction of Azoxybenzenes	1800
31.34.10.1.3	Method 3: Reduction of Azoarenes	1800
31.34.10.1.3.1	Variation 1: Using Zinc	1801
31.34.10.1.3.2	Variation 2: Using Zinc and Ammonium Formate in an Ionic Liquid	1801
31.34.10.1.3.3	Variation 3: Using Sodium Amalgam	1802
31.34.10.1.3.4	Variation 4: Using Samarium(II) Iodide	1802
31.34.10.1.3.5	Variation 5: By Hydrogenation	1802
31.34.10.1.3.6	Variation 6: Using Borane in Tetrahydrofuran	1803
31.34.10.1.3.7	Variation 7: Using Sodium Borohydride–Iodine or Sodium Borohydride–Ammonium Iodide	1804
31.34.10.1.3.8	Variation 8: Using Lithium Aluminum Hydride	1804
31.34.10.1.3.9	Variation 9: Using Tributyltin Hydride	1804
31.34.10.1.3.10	Variation 10: Using Tellurium Reagents	1805
31.34.10.1.3.11	Variation 11: Using Hydrazine	1805
31.34.10.1.3.12	Variation 12: Using Raney Nickel and Hydrazinium Monoformate	1806
31.34.10.1.3.13	Variation 13: Using Zinc Dust and Hydrazinium Monoformate	1807
31.34.10.1.3.14	Variation 14: Using Hydrazine and Hydrated Zirconium(IV) Oxide	1808

31.34.10.1.3.15	Variation 15:	Using Sodium Dithionite with Dioctylviologen as an Electron-Transfer Catalyst	1808
31.34.10.1.3.16	Variation 16:	Using Formamidinesulfinic Acid	1809
31.34.10.1.4	Method 4:	Reduction of Nitrosobenzenes	1809
31.34.10.1.5	Method 5:	N-Arylation	1809
31.34.10.1.5.1	Variation 1:	Copper(I)-Catalyzed N-Arylation of 1,2-Bis(<i>tert</i> -butoxy-carbonyl)-1-phenylhydrazines	1809
31.34.10.1.5.2	Variation 2:	Palladium-Catalyzed N-Arylation of 1-Aryl-1-(<i>tert</i> -butoxy-carbonyl)hydrazines	1810
31.34.10.1.5.3	Variation 3:	N-Arylation of Aryl- and Hetarylhydrazines by Arenes Possessing Activated Leaving Groups	1811
31.34.10.1.6	Method 6:	Electrophilic Amination of Primary Anilines Using <i>N</i> -Aryl- <i>O</i> -(diphenylphosphoryl)hydroxylamines	1812
31.34.10.1.7	Method 7:	Treatment of Phenols with Phenylhydrazine and Sodium Hydrogen Sulfite	1812
31.34.10.1.8	Methods 8:	Miscellaneous Methods	1813
31.34.11	Product Subclass 11: 1-Alkyl-1,2-diarylhydrazines		1813
31.34.11.1	Synthesis of Product Subclass 11		1813
31.34.11.1.1	Method 1:	Addition of Organometallic Reagents to Azobenzenes	1813
31.34.11.1.2	Method 2:	Arylation of 1-Alkyl-1-arylhydrazines	1814
31.34.11.1.3	Methods 3:	Miscellaneous Methods	1814
31.34.12	Product Subclass 12: 1,2-Dialkyl-1,2-diarylhydrazines		1815
31.34.12.1	Synthesis of Product Subclass 12		1815
31.34.12.1.1	Method 1:	Addition of Organometallic Reagents to Azobenzenes Followed by Alkylation	1815
31.34.12.1.2	Method 2:	Alkylation of Azobenzene Metal Adducts	1815
31.34.12.1.3	Methods 3:	Miscellaneous Methods	1816
31.34.13	Product Subclass 13: 1,1,2-Triarylhydrazines		1816
31.34.13.1	Synthesis of Product Subclass 13		1816
31.34.13.1.1	Method 1:	Addition of Organometallic Reagents to Azobenzenes	1816
31.34.13.1.2	Method 2:	Arylation of 1,1-Diarylhydrazines	1816
31.34.14	Product Subclass 14: 1-Alkyl-1,2,2-triarylhydrazines		1816
31.34.14.1	Synthesis of Product Subclass 14		1817
31.34.14.1.1	Method 1:	Addition of Aryllithium Reagents to Azoarenes Followed by Addition of a Primary Alkyl Iodide	1817
31.34.15	Product Subclass 15: 1,1,2,2-Tetraarylhydrazines		1817
31.34.15.1	Synthesis of Product Subclass 15		1817
31.34.15.1.1	Method 1:	Oxidative Coupling of Diarylamines	1817
31.34.15.1.1.1	Variation 1:	Copper(II)-Promoted Oxidative Coupling of Secondary Arylamines Using Oxygen	1817
31.34.15.1.1.2	Variation 2:	Oxidative Dimerization of Amines Using Potassium Permanganate	1818
31.34.15.1.1.3	Variation 3:	Oxidative Dimerization of Amines Using Lead(IV) Oxide	1818

31.35 Product Class 35: Aryl Azides

S. Bräse, D. Keck

31.35	Product Class 35: Aryl Azides	1827
31.35.1	Synthesis of Product Class 35	1827
31.35.1.1	Method 1: Synthesis from Aryl Organometallic Compounds	1827
31.35.1.1.1	Variation 1: From Aryllithium Compounds	1827
31.35.1.1.2	Variation 2: From Arylthallium Compounds	1828
31.35.1.1.3	Variation 3: From Aryllead Compounds	1829
31.35.1.2	Method 2: Synthesis by Nucleophilic Substitution of Aryl Halides	1830
31.35.1.2.1	Variation 1: From Activated Arenes	1830
31.35.1.2.2	Variation 2: By Copper-Catalyzed Reactions	1830
31.35.1.3	Method 3: Synthesis by Modification of Triazenes	1831
31.35.1.4	Method 4: Synthesis from Tetrazenes	1832
31.35.1.5	Method 5: Synthesis from Arenediazonium Salts	1832
31.35.1.6	Method 6: Synthesis from Hydrazines and Related Compounds	1834
31.35.1.7	Method 7: Synthesis from Anilines and Related Compounds	1835
31.35.1.8	Method 8: Synthesis from Nitrosoarenes	1835
31.35.1.9	Method 9: Synthesis by Rearrangement	1836
31.35.2	Applications of Product Class 35 in Organic Synthesis	1836
31.35.2.1	Method 1: Reactions with All-Carbon Functional Groups	1837
31.35.2.2	Method 2: Reactions with Heteroatom-Containing Groups	1839

31.36 Product Class 36: Aryltriazenes, Aryltetrazenes, and Related Compounds

S. Bräse and T. Muller

31.36	Product Class 36: Aryltriazenes, Aryltetrazenes, and Related Compounds	1845
31.36.1	Product Subclass 1: Aryltetrazenes	1846
31.36.1.1	Synthesis of Product Subclass 1	1846
31.36.1.1.1	Method 1: Dimerization of Hydrazines and Hydrazones	1846
31.36.1.1.2	Method 2: Reaction between Hydrazides and Hydrazones	1847
31.36.1.1.3	Method 3: Reaction of Azo Compounds with Hydrazones	1848
31.36.2	Product Subclass 2: Aryltriazenes	1849
31.36.2.1	Synthesis of Product Subclass 2	1849
31.36.2.1.1	Method 1: Synthesis from <i>N</i> -Nitrosoureas or Aryl Isocyanates	1849
31.36.2.1.2	Method 2: Synthesis from Aryl Azides	1851
31.36.2.1.3	Method 3: Synthesis from Alkyl or Acyl Azides and Arylating Agents	1853
31.36.2.1.4	Method 4: Synthesis from Arenediazonium Salts	1854
31.36.2.1.5	Method 5: Ring Opening of Cyclic Compounds	1856
31.36.2.1.6	Method 6: Modification of Triazenes by Formation of Complexes with Organometallic Reagents and Triazene Salts	1856
31.36.2.1.7	Method 7: Exchange of the Amine Functional Group in Triazenes	1858
31.36.2.1.8	Method 8: <i>N</i> -Alkylation of Aryltriazenes	1859
31.36.2.1.9	Method 9: <i>N</i> -Acylation of Aryltriazenes	1860

31.36.2.1.10	Method 10: Deacylation of Aryltriazenes	1860
31.36.3	Product Subclass 3: Aryltriazene <i>N</i>-Oxides	1862
31.36.3.1	Synthesis of Product Subclass 3	1862
31.36.3.1.1	Method 1: Synthesis from Diazonium Salts and Hydroxylamines	1862
31.36.3.1.2	Method 2: Synthesis from Hydrazines and Nitroso Compounds	1863
31.36.4	Product Subclass 4: Aryltetrazenes	1863
31.36.4.1	Synthesis of Product Subclass 4	1864
31.36.4.1.1	Method 1: Dimerization of Hydrazines	1864
31.36.4.1.2	Method 2: Modification of Tetrazenes	1865
31.36.4.1.3	Method 3: Reaction of Diazonium Salts with Hydrazines	1866
31.36.5	Product Subclass 5: Arylpentazenes	1867
31.36.5.1	Synthesis of Product Subclass 5	1867
31.36.5.1.1	Method 1: Reaction of Arenediazonium Salts	1867
31.36.6	Product Subclass 6: Arylhexazenes	1868
31.36.6.1	Synthesis of Product Subclass 6	1868
31.36.6.1.1	Method 1: Synthesis from Arenediazonium Salts and Hydrazines	1868
31.36.6.1.2	Method 2: Synthesis from 1,3-Diaryltriazenes	1869
31.37	Product Class 37: <i>N</i>-Phosphinoarylamines M. Alajarín, C. López-Leonardo, and J. Berná	
31.37	Product Class 37: <i>N</i>-Phosphinoarylamines	1873
31.37.1	Product Subclass 1: <i>N</i>-Monophosphinoarylamines	1873
31.37.1.1	Synthesis of Product Subclass 1	1873
31.37.1.1.1	Method 1: Aminolysis of Chlorophosphines	1873
31.37.1.1.1.1	Variation 1: Stepwise Using Dichlorophosphines	1877
31.37.1.1.1.2	Variation 2: Using Silylamines	1877
31.37.1.1.2	Method 2: Amino Interchange	1878
31.37.1.1.3	Methods 3: Miscellaneous Syntheses	1878
31.37.2	Product Subclass 2: <i>N,N</i>-Diphosphinoarylamines	1879
31.37.2.1	Synthesis of Product Subclass 2	1879
31.37.2.1.1	Method 1: Aminolysis of Chlorodiphenylphosphine	1879
31.37.2.1.2	Method 2: Synthesis Using Alkali Metal <i>N</i> -Phosphinoarylamides	1880
31.37.3	Product Subclass 3: Bis(arylamino)phosphines	1881
31.37.3.1	Synthesis of Product Subclass 3	1881
31.37.3.1.1	Method 1: Aminolysis of Dichlorophosphines	1881
31.37.3.1.2	Method 2: Amino Interchange	1882

31.38 Product Class 38: Cyclic Arylamines

P. J. Stevenson

31.38	Product Class 38: Cyclic Arylamines	1885
31.38.1	Product Subclass 1: Cyclic Monoarylamines	1886
31.38.1.1	Synthesis of Product Subclass 1	1886
31.38.1.1.1	Method 1: Formation of One C(sp ³)—N and Two C—C Bonds	1886
31.38.1.1.1.1	Variation 1: Condensation of Two Aldehydes with an Arylamine	1886
31.38.1.1.1.2	Variation 2: Condensation between an Aldehyde and an Arylamine in the Presence of 1 <i>H</i> -Benzotriazole	1886
31.38.1.1.1.3	Variation 3: Reaction of an Arylamine with Two Equivalents of a Masked Aldehyde	1887
31.38.1.1.1.4	Variation 4: Intermolecular Condensation of an Arylamine, an Aldehyde, and an Alkene	1888
31.38.1.1.1.5	Variation 5: Intramolecular Condensations between Anilines and Hex-5-enals	1889
31.38.1.1.2	Method 2: Formation of One C(sp ³)—N and One C—C Bond	1890
31.38.1.1.2.1	Variation 1: 1-Alkyl-3-(trifluoromethyl)-2,3-dihydro-1 <i>H</i> -indol-3-ols by Reactions of Alkoxyoxiranes with <i>N</i> -Alkylanilines	1890
31.38.1.1.2.2	Variation 2: Tetrahydroquinolines by the Cycloaddition of <i>ortho</i> -Azaxylylenes	1891
31.38.1.1.2.3	Variation 3: Tetrahydroquinolines by the Annulation of 2-Iodoanilines	1892
31.38.1.1.3	Method 3: Formation of Two C—C Bonds	1893
31.38.1.1.3.1	Variation 1: Intramolecular Diels–Alder Reactions of Furan-2-amines and Diazin-2-amines	1893
31.38.1.1.3.2	Variation 2: Intermolecular Diels–Alder Reactions between Imines and Alkenes	1894
31.38.1.1.3.3	Variation 3: Diels–Alder Reactions of <i>N,N</i> -, <i>O,N</i> -, or <i>S,N</i> -Acetals Derived from Arylamines with Alkenes	1895
31.38.1.1.3.4	Variation 4: Reactions of Nitrones with Electron-Deficient Allenes	1896
31.38.1.1.4	Method 4: Nuncatalytic Ring Closure via Formation of a C(sp ²)—N Bond	1897
31.38.1.1.4.1	Variation 1: Benzyl-2,3-dihydro-1 <i>H</i> -indoles by Aryl Radical Cyclizations onto Imines	1897
31.38.1.1.4.2	Variation 2: Reactions of Aryllithiums with Electrophilic Nitrogen Compounds	1897
31.38.1.1.4.3	Variation 3: Intramolecular Nucleophilic Aromatic Substitution Reactions	1898
31.38.1.1.5	Method 5: Catalytic Ring Closure via the Formation of a C(sp ²)—N Bond	1899
31.38.1.1.5.1	Variation 1: Palladium-Catalyzed <i>N</i> -Arylation Reactions	1900
31.38.1.1.5.2	Variation 2: Copper-Catalyzed Intramolecular <i>N</i> -Arylation Reactions	1901
31.38.1.1.5.3	Variation 3: Nickel-Catalyzed Intramolecular <i>N</i> -Arylation Reactions	1902
31.38.1.1.6	Method 6: Ring Closure via the Formation of a C(sp ³)—N Bond	1903
31.38.1.1.6.1	Variation 1: Carboamination of Alkenes	1903
31.38.1.1.6.2	Variation 2: Tandem Reduction of a Nitro Group and Cyclization of the Resulting Amine	1904
31.38.1.1.6.3	Variation 3: Intramolecular <i>N</i> -Alkylation with Acetamides or Tosylamides	1906
31.38.1.1.6.4	Variation 4: Intramolecular <i>N</i> -Alkylation of Alcohols	1907
31.38.1.1.6.5	Variation 5: Intramolecular <i>N</i> -Alkylation of Epoxides	1907

31.38.1.1.7	Method 7:	Ring Closure via the Formation of a C(sp ²)—C(sp ²) Bond	1908
31.38.1.1.7.1	Variation 1:	Synthesis by Alkene Metathesis	1908
31.38.1.1.7.2	Variation 2:	Electrophilic Acylation	1909
31.38.1.1.7.3	Variation 3:	Synthesis by the Intramolecular Electrophilic Substitution of Propargyl Trimethylsilyl Ethers	1909
31.38.1.1.7.4	Variation 4:	Intramolecular Heck Reactions	1910
31.38.1.1.8	Method 8:	Ring Closure via the Formation of a C(sp ³)—C(sp ³) Bond	1911
31.38.1.1.8.1	Variation 1:	Cyclization of Imines	1911
31.38.1.1.9	Method 9:	Ring Closure via the Formation of a C(sp ²)—C(sp ³) Bond	1912
31.38.1.1.9.1	Variation 1:	Dieckmann Cyclization of Diesters	1912
31.38.1.1.9.2	Variation 2:	Intramolecular Electrophilic Substitution	1913
31.38.1.1.9.3	Variation 3:	Radical Cyclization	1913
31.38.1.1.9.4	Variation 4:	Palladium-Catalyzed Cyclizations of <i>N</i> -Allyl-2-iodoanilines	1915
31.38.1.1.9.5	Variation 5:	Cyclization of <i>N,N</i> -Diallyl-2-bromoanilines	1917
31.38.1.1.9.6	Variation 6:	Zirconium-Mediated Cyclizations Involving Arynes	1918
31.38.1.1.10	Method 10:	Synthesis by Ring Transformation	1919
31.38.1.1.10.1	Variation 1:	Migration to an Electron-Deficient Nitrogen Center	1919
31.38.1.1.11	Method 11:	Synthesis by Substituent Modification	1920
31.38.1.1.11.1	Variation 1:	Asymmetric Lithiation Followed by Trapping with Electrophiles	1920
31.38.1.1.11.2	Variation 2:	Electrophilic Substitution	1921
31.38.1.1.12	Method 12:	Synthesis from Other Aromatic Heterocycles	1921
31.38.1.1.12.1	Variation 1:	Reduction of Aromatic Heterocycles	1922
31.38.1.1.12.2	Variation 2:	Oxidative Cleavage of C—C Bonds	1923
31.38.2	Product Subclass 2: Cyclic Diarylamines		1924
31.38.2.1	Synthesis of Product Subclass 2		1924
31.38.2.1.1	Method 1:	Formation of Two C(sp ²)—C(sp ³) Bonds	1924
31.38.2.1.2	Method 2:	Formation of One C(sp ²)—N Bond	1924
31.38.2.1.3	Method 3:	Formation of One C(sp ²)—C(sp ²) Bond	1925
31.38.2.1.4	Method 4:	Formation of One C(sp ²)—C(sp ³) Bond	1925
31.38.2.1.5	Method 5:	Synthesis from Aromatic Heterocycles	1926
31.38.2.1.5.1	Variation 1:	Reactions of Acridines with Nucleophiles	1926
31.38.2.1.5.2	Variation 2:	Reduction of Acridines	1927
31.38.3	Product Subclass 3: Cyclic Arenediamines		1927
31.38.3.1	Synthesis of Product Subclass 3		1927
31.38.3.1.1	Method 1:	Formation of Two C(sp ²)—N(sp ³) Bonds	1927
31.38.3.1.2	Method 2:	Formation of Two C(sp ³)—N(sp ³) Bonds	1928
31.38.3.1.2.1	Variation 1:	Reactions of Aromatic Diamines with Ketones	1928
31.38.3.1.2.2	Variation 2:	1,2,3,4-Tetrahydroquinoxalines by Reactions of Benzene-1,2-diamine with (<i>Z</i>)-But-2-ene-1,4-diol or Its Derivatives	1928
31.38.3.1.2.3	Variation 3:	Annulations with Oxirane-2-carbonitriles	1929
31.38.3.1.2.4	Variation 4:	Annulation with α,ω -Dibromoalkanes	1929
31.38.4	Product Subclass 4: 5,10-Dihydrophenazines		1930
31.38.4.1	Synthesis of Product Subclass 4		1930
31.38.4.1.1	Method 1:	Formation of Two C(sp ²)—N(sp ³) Bonds	1930

31.39 Product Class 39: Arylphosphonic Acids and Derivatives

I. B. Gorrell and T. P. Kee

31.39	Product Class 39: Arylphosphonic Acids and Derivatives	1939
31.39.1	Synthesis of Product Class 39	1939
31.39.1.1	Synthesis via P—C Bond Formation	1939
31.39.1.1.1	Method 1: Reactions of Nucleophilic Phosphorus	1939
31.39.1.1.1.1	Variation 1: The Arbuzov Reaction and Related Reactions	1939
31.39.1.1.1.2	Variation 2: Synthesis from Diazonium Salts	1944
31.39.1.1.2	Method 2: Reactions of Electrophilic Phosphorus	1946
31.39.1.1.2.1	Variation 1: Reactions of Phosphorus(V) Compounds with Organometallic Reagents	1946
31.39.1.1.2.2	Variation 2: Reactions of Phosphorus(III) Compounds with Organometallic Reagents	1949
31.39.1.1.2.3	Variation 3: Preparation via a Modified Friedel–Crafts Procedure	1951
31.39.1.1.2.4	Variation 4: The Phospho-Fries Rearrangement	1953
31.39.1.1.2.5	Variation 5: Direct Phosphonation of Arenes with Phosphorus Pentoxide or Pentasulfide	1956
31.39.1.1.3	Method 3: Synthesis via Free-Radical Phosphonation	1958
31.39.1.2	Synthesis via Modification of a Preformed P—C Bond Containing Framework	1958
31.39.1.2.1	Method 1: Synthesis via Transformations of Existing Arylphosphonic Acids	1958
31.39.1.2.2	Method 2: Oxidation of Arylphosphinic Acids	1960

31.40 Product Class 40: Arylphosphinic Acids and Derivatives

H.-J. Cristau and D. Virieux

31.40	Product Class 40: Arylphosphinic Acids and Derivatives	1963
31.40.1	Product Subclass 1: Arylphosphinic Acids and Derivatives with a P=O Bond	1963
31.40.1.1	Synthesis of Product Subclass 1	1963
31.40.1.1.1	Method 1: Arylphosphinic Halides from Trivalent Arylphosphorus Halides	1963
31.40.1.1.1.1	Variation 1: Oxidation of Aryl(monochloro)phosphines	1963
31.40.1.1.1.2	Variation 2: Alkylation of Aryldichlorophosphines	1964
31.40.1.1.1.3	Variation 3: Addition of Aryldichlorophosphines to Activated C=C Bonds	1965
31.40.1.1.1.4	Variation 4: α -Functional Alkylation of Aryldichlorophosphines	1966
31.40.1.1.2	Method 2: Arylphosphinic Halides from Tetracoordinated Phosphorus Acids and Their Derivatives	1968
31.40.1.1.2.1	Variation 1: Arylphosphinic Halides from Phosphonic Dihalides	1968
31.40.1.1.2.2	Variation 2: Arylphosphinic Halides from Phosphinic Acids and Esters	1969
31.40.1.1.2.3	Variation 3: Arylphosphinic Halides from Hydrogenophosphine Oxides	1970
31.40.1.1.3	Method 3: Arylphosphinic Halides from Pentacoordinated Phosphorus Compounds	1972
31.40.1.1.4	Method 4: Arylphosphinic Acids from Phosphorus(III) Derivatives	1973

31.40.1.1.4.1	Variation 1:	Arylphosphinic Acids from Phosphorus(III) Halides by Reaction with Arenediazonium Salts	1973
31.40.1.1.4.2	Variation 2:	Arylphosphinic Acids from Phosphorus(III) Halides by Reaction with Organometallic Compounds	1974
31.40.1.1.4.3	Variation 3:	Arylphosphinic Acids from Phosphorus(III) Halides by α -Aminoalkylation	1975
31.40.1.1.5	Method 5:	Arylphosphinic Acids from Tetracoordinated Phosphorus Derivatives	1978
31.40.1.1.5.1	Variation 1:	Arylphosphinic Acids from Tetracoordinated Phosphorus Halides	1978
31.40.1.1.5.2	Variation 2:	Arylphosphinic Acids from Tetracoordinated Phosphorus Acids or Their Derivatives	1978
31.40.1.1.5.3	Variation 3:	Arylphosphinic Acids from Phosphine Oxides	1980
31.40.1.1.6	Method 6:	Arylphosphinic Esters from Phosphorus(III) Derivatives	1981
31.40.1.1.6.1	Variation 1:	Arylphosphinic Esters from Aryldichlorophosphines by Reactions with Enolizable Ketones	1981
31.40.1.1.6.2	Variation 2:	Arylphosphinic Esters from Phosphorus(III) Esters by Arbuzov Reaction or Rearrangement	1984
31.40.1.1.6.3	Variation 3:	Arylphosphinic Esters from Phosphines and Polyphosphines	1987
31.40.1.1.7	Method 7:	Arylphosphinic Esters from Tetracoordinated Phosphorus Derivatives	1987
31.40.1.1.7.1	Variation 1:	Arylphosphinic Esters from Tetracoordinated Phosphorus Halides by Reaction with Organometallic Compounds	1987
31.40.1.1.7.2	Variation 2:	Arylphosphinic Esters by α -Hydroxyalkylation of Aryl(hydrogeno)phosphinates	1988
31.40.1.1.7.3	Variation 3:	α -Aminoalkylation of Aryl(hydrogeno)phosphonates	1991
31.40.1.1.7.4	Variation 4:	Arylphosphinic Esters by Reaction of Hydrogenophosphinates with Alkenes	1993
31.40.1.1.7.5	Variation 5:	Arylphosphinic Esters by Alkylation of Hydrogenophosphinic Esters	1995
31.40.1.1.7.6	Variation 6:	Arylphosphinic Esters or Acids by Arylation of Hydrogenophosphinates	1995
31.40.1.1.7.7	Variation 7:	Arylphosphinic Esters by Hydrophosphination of Alkynes ...	1998
31.40.1.1.8	Method 8:	Arylphosphinic Esters from Phosphinic Acids	1998
31.40.1.1.9	Method 9:	Symmetrical Arylphosphinic Anhydrides from Tetracoordinated Phosphorus Acids and Their Derivatives	2000
31.40.1.1.9.1	Variation 1:	Symmetrical Arylphosphinic Anhydrides from Diarylphosphine Dioxides	2000
31.40.1.1.9.2	Variation 2:	Symmetrical Arylphosphinic Anhydrides from Arylphosphinic Acids and Their Derivatives	2000
31.40.1.1.10	Method 10:	Mixed Arylphosphinic–Carboxylic Anhydrides from Phosphinic Acids and Their Derivatives	2001
31.40.1.1.10.1	Variation 1:	Mixed Arylphosphinic–Carboxylic Anhydrides by Oxidation of Arylphosphinous–Carboxylic Anhydrides	2001
31.40.1.1.10.2	Variation 2:	Mixed Arylphosphinic–Carboxylic Anhydrides from Phosphinic Acids and Their Derivatives	2001
31.40.1.1.11	Method 11:	Synthesis of Arylphosphinothioic S-Esters	2002

31.40.1.1.11.1	Variation 1:	Synthesis of Arylphosphinothioic S-Esters from Hydrogenophosphine Oxides	2002
31.40.1.1.11.2	Variation 2:	Synthesis of Arylphosphinothioic S-Esters from Arylphosphinic Chlorides	2003
31.40.1.1.12	Method 12:	<i>P</i> -Arylphosphinic Amides and Their Analogues from Phosphorus(III) Derivatives	2003
31.40.1.1.12.1	Variation 1:	<i>N</i> -Alkylidene- <i>P</i> -arylphosphinic Amides from Diaryl(chloro)phosphines and Oximes	2003
31.40.1.1.12.2	Variation 2:	<i>P</i> -Arylphosphinic Amides by Reaction of Electrophiles with Dichlorophosphines	2005
31.40.1.1.12.3	Variation 3:	<i>P</i> -Arylphosphinic Amides by Reactions of Aminophosphonites	2006
31.40.1.1.12.4	Variation 4:	<i>P</i> -Arylphosphinic Amides by Oxidation of Aminophosphines	2007
31.40.1.1.13	Method 13:	<i>P</i> -Arylphosphinic Amides and Their Analogues from Tetracoordinated Phosphorus Derivatives	2008
31.40.1.1.13.1	Variation 1:	<i>P</i> -Arylphosphinic Amides and Their Analogues from Phosphinic Chlorides	2008
31.40.1.1.13.2	Variation 2:	<i>P</i> -Arylphosphinic Amides from Phosphonamidic Chlorides	2009
31.40.1.1.14	Method 14:	<i>P</i> -Arylphosphinic Amides from Pentacoordinated Phosphorus Derivatives	2009
31.40.2	Product Subclass 2: Arylphosphinothioic and Arylphosphinoselenoic O-Acids and Derivatives		2010
31.40.2.1	Synthesis of Product Subclass 2		2010
31.40.2.1.1	Method 1:	Arylphosphinothioic and Arylphosphinoselenoic Halides from Phosphorus Precursors without a Sulfur or Selenium Atom	2010
31.40.2.1.1.1	Variation 1:	Arylphosphinothioic or Arylphosphinoselenoic Halides by Sulfuration or Selenation of Tricoordinated Phosphorus Chlorides	2010
31.40.2.1.1.2	Variation 2:	Arylphosphinothioic Halides by a One-Pot Arylation–Sulfuration Reaction	2011
31.40.2.1.1.3	Variation 3:	Arylphosphinothioic Halides by Thioallylation–Allylic Rearrangement	2011
31.40.2.1.1.4	Variation 4:	Arylphosphinoselenoic Halides by a One-Pot Selenation–Grignard Reaction from Tricoordinated Phosphorus Compounds	2011
31.40.2.1.1.5	Variation 5:	Arylphosphinothioic Halides by Sulfuration of Tetracoordinated Phosphorus Compounds	2012
31.40.2.1.2	Method 2:	Arylphosphinothioic or Arylphosphinoselenoic Halides from Phosphorus Precursors Containing a Sulfur or Selenium Atom	2013
31.40.2.1.2.1	Variation 1:	Halogenation of Tetracoordinated Phosphinothioic or Phosphinoselenoic Derivatives	2013
31.40.2.1.2.2	Variation 2:	Oxidation of Hydrogenophosphine Sulfides	2014
31.40.2.1.2.3	Variation 3:	Oxidation of Diphosphine Disulfides	2014
31.40.2.1.3	Method 3:	Arylphosphinothioic O-Acids from Phosphorus Precursors Lacking Sulfur Atoms	2015

31.40.2.1.4	Method 4:	Arylphosphinothioic or Arylphosphinoselenoic O-Acids from Phosphorus Precursors Containing a Sulfur or Selenium Atom	2016
31.40.2.1.5	Method 5:	Arylphosphinothioic or Arylphosphinoselenoic O-Esters from Phosphorus Precursors Lacking a Sulfur or Selenium Atom	2016
31.40.2.1.5.1	Variation 1:	Sulfuration or Selenation of Tricoordinated Phosphorus Compounds	2016
31.40.2.1.5.2	Variation 2:	Sulfuration or Selenation of Tetracoordinated Phosphorus Compounds	2018
31.40.2.1.5.3	Variation 3:	Sulfuration of Dicoordinated Phosphorus Compounds	2019
31.40.2.1.6	Method 6:	Arylphosphinothioic or Arylphosphinoselenoic O-Acids or O-Esters from Phosphorus Precursors with a Sulfur or Selenium Atom	2019
31.40.2.1.6.1	Variation 1:	Synthesis from Arylphosphinothioic or Arylphosphinoselenoic Chlorides	2019
31.40.2.1.6.2	Variation 2:	Synthesis of Phosphinothioic O-Esters by Activation of Acids	2020
31.40.2.1.6.3	Variation 3:	Reaction of Hydrogenophosphinothioates	2021
31.40.2.1.6.4	Variation 4:	Ring Opening of Cyclic Derivatives	2021
31.40.2.1.6.5	Variation 5:	α -Alkylation of Phosphinothioates	2022
31.40.2.1.6.6	Variation 6:	Other Methods Involving Rearrangements	2022

31.41 Product Class 41: Arylphosphine Oxides

C. A. Ramsden

31.41	Product Class 41: Arylphosphine Oxides	2035
31.41.1	Product Subclass 1: Symmetrical and Racemic Arylphosphine Oxides ...	2035
31.41.1.1	Synthesis of Product Subclass 1	2035
31.41.1.1.1	Method 1: Synthesis from Phosphoryl Chloride	2035
31.41.1.1.2	Method 2: Synthesis from Phosphonic Acid Esters	2036
31.41.1.1.2.1	Variation 1: By Reaction with Organometallic Reagents	2036
31.41.1.1.2.2	Variation 2: By Rearrangement	2037
31.41.1.1.3	Method 3: Synthesis from Phosphinic Chlorides	2037
31.41.1.1.4	Method 4: Synthesis from Phosphinic Acid Esters	2038
31.41.1.1.4.1	Variation 1: By Reaction with Organometallic Reagents	2038
31.41.1.1.4.2	Variation 2: By Rearrangement	2040
31.41.1.1.5	Method 5: Synthesis from Halophosphines (Phosphinous Halides)	2040
31.41.1.1.6	Method 6: Synthesis from Phosphinous Acids and Esters	2041
31.41.1.1.6.1	Variation 1: Michaelis–Arbuzov Reaction of Alkyl Phosphinites	2041
31.41.1.1.6.2	Variation 2: By Alkylation of Phosphinite Anions	2042
31.41.1.1.6.3	Variation 3: By Metal-Catalyzed Coupling Reactions	2043
31.41.1.1.6.4	Variation 4: By 1,2-Hydrophosphination of Unsaturated Compounds ...	2044
31.41.1.1.6.5	Variation 5: By Rearrangement of Allyl Phosphinites	2045
31.41.1.1.7	Method 7: Synthesis from Phosphonium Salts	2046
31.41.1.1.8	Method 8: Synthesis from Phosphines	2047
31.41.2	Product Subclass 2: Optically Active Arylphosphine Oxides	2048
31.41.2.1	Synthesis of Product Subclass 2	2049

31.41.2.1.1	Method 1:	Nucleophilic Displacement at Phosphorus	2049
31.41.2.1.2	Method 2:	Alkylation at Phosphorus	2050
31.41.2.1.3	Method 3:	Optical Resolution	2050
31.41.2.1.4	Method 4:	Kinetic Resolution	2053
31.42	Product Class 42: Arylphosphines and Derivatives		
	P. J. Murphy and H. Böckemeier		
31.42	Product Class 42: Arylphosphines and Derivatives		2057
31.42.1	Synthesis of Product Class 42		2057
31.42.1.1	Method 1:	Electrochemical Synthesis	2057
31.42.1.2	Method 2:	Nickel-Catalyzed Coupling of Arylphosphines and Aryl Trifluoromethanesulfonates	2059
31.42.1.3	Method 3:	Synthesis from Metalated Arylphosphines	2060
31.42.1.4	Method 4:	Reaction of Halophosphines with Organometallic Reagents	2065
31.42.1.5	Method 5:	Preparation of Chiral Phosphines by Substitution of Arylphosphinites	2073
31.42.1.6	Method 6:	Reduction of Arylphosphine Oxides	2074
31.43	Product Class 43: Arylphosphonium Salts and Derivatives		
	J. C. Tebby and D. W. Allen		
31.43	Product Class 43: Arylphosphonium Salts and Derivatives		2083
31.43.1	Synthesis of Product Class 43		2083
31.43.1.1	Method 1:	Direct Quaternization of Arylphosphines by Nucleophilic Substitution	2083
31.43.1.1.1	Variation 1:	Quaternization by Alkyl Halides, Alkyl Trifluoromethane- sulfonates, and Activated Aryl Halides	2083
31.43.1.1.2	Variation 2:	Quaternization by Quaternary Ammonium Salts	2086
31.43.1.1.3	Variation 3:	Quaternization by Protonated Alcohols, Esters, and Oxonium Salts	2086
31.43.1.1.4	Variation 4:	Quaternization by Acetals, Epoxides, and Other Cyclic Compounds	2087
31.43.1.2	Method 2:	Quaternization of Arylphosphines by Addition	2088
31.43.1.2.1	Variation 1:	Addition to Alkenes	2088
31.43.1.2.2	Variation 2:	Addition to Alkynes	2089
31.43.1.2.3	Variation 3:	Addition to Carbonyl, Imino, and Iminium Groups	2090
31.43.1.2.4	Variation 4:	Addition to Carbocations	2090
31.43.1.3	Method 3:	Arylation, Alkenylation, and Alkynylation of Tertiary Phosphines	2091
31.43.1.3.1	Variation 1:	Catalytic Quaternization by Aryl and Vinyl Halides	2091
31.43.1.3.2	Variation 2:	Quaternization by Iodonium Salts	2093
31.43.1.3.3	Variation 3:	Quaternization by Arynes	2094
31.43.1.3.4	Variation 4:	Quaternization by Radicals	2094
31.43.1.4	Method 4:	Quaternization by Electrochemical Methods	2094

31.43.1.5	Method 5:	Interconversion and Intramolecular Cyclization of Phosphonium Salts	2095
31.43.1.6	Methods 6:	Miscellaneous Methods	2096
31.43.1.6.1	Variation 1:	Quaternization of Phosphines by Acyl Halides	2096
31.43.1.6.2	Variation 2:	Quaternization of Phosphides and Chlorophosphines	2097
31.43.1.6.3	Variation 3:	Conversions from Phosphonium Ylides and Vinylphosphonium Salts	2097
31.43.1.6.4	Variation 4:	Generation of Specific Counterions	2098
31.44	Product Class 44: P-Heteroatom-Substituted Arylphosphines M. Alajarín, C. López-Leonardo, and J. Berná		
31.44	Product Class 44: P-Heteroatom-Substituted Arylphosphines		2105
31.44.1	Product Subclass 1: Aryl(halo)phosphines and Aryl(dihalo)phosphines		2106
31.44.1.1	Synthesis of Product Subclass 1		2106
31.44.1.1.1	Method 1:	Friedel–Crafts Reaction of Arenes with Phosphorus Trihalides	2106
31.44.1.1.2	Method 2:	Aryl(halo)phosphines by Reaction of Aryl(dihalo)phosphines with Aliphatic Hydrocarbons	2109
31.44.1.1.3	Method 3:	Halogenation of Phosphines	2110
31.44.1.1.4	Method 4:	Nucleophilic Substitution of Halogens with Organometallic Reagents	2112
31.44.1.1.5	Method 5:	Halogen Exchange of Chlorophosphines	2113
31.44.1.1.6	Method 6:	Reaction of Aminophosphines and Diaminophosphines with Hydrogen Halides	2114
31.44.1.1.7	Method 7:	Reduction of Aryl(trihalo)phosphonium Salts	2115
31.44.1.1.8	Method 8:	Reaction of Arylphosphinous and Arylphosphonous Acids and Their Esters with Halogens and Phosphorus Trihalides	2116
31.44.1.1.9	Method 9:	Reduction of Halophosphoranes	2117
31.44.1.1.10	Method 10:	Cleavage of P–C Bonds in Bis(phosphino)methanes	2117
31.44.1.1.11	Method 11:	Cleavage of the P–P Bond of Diphosphines	2118
31.44.1.1.12	Method 12:	Addition Reactions of Phosphaalkenes and Related Compounds	2118
31.44.2	Product Subclass 2: Arylphosphinous Esters, Arylphosphonous Esters, and Thio Analogues		2119
31.44.2.1	Synthesis of Product Subclass 2		2119
31.44.2.1.1	Method 1:	Reaction of Aryl(halo)phosphines, Aryl(dihalo)phosphines, Alkoxy(aryl)(halo)phosphines, or (Alkylsulfanyl)(aryl)(halo)phosphines with Alcohols or Thiols	2119
31.44.2.1.2	Method 2:	Reaction of Aryl(dihalo)phosphines with Epoxides	2121
31.44.2.1.3	Method 3:	Reaction of Aryl(dihalo)phosphines with Cyclic Siloxanes and Related Species	2122
31.44.2.1.4	Method 4:	Reaction of Aryl(halo)phosphines and Aryl(dihalo)phosphines with Dithiocarbonates	2123
31.44.2.1.5	Method 5:	Reaction of Primary Arylphosphines with Dialkyl Disulfides	2123
31.44.2.1.6	Method 6:	Reaction of Chlorophosphates and Dichlorophosphates with Organometallic Reagents	2124

31.44.2.1.7	Method 7:	Reaction of Phosphites with Organometallic Reagents	2125
31.44.2.1.8	Method 8:	Alcoholysis of the P—N Bond of Aminophosphines	2126
31.44.2.1.9	Method 9:	Reduction of Phosphinothioates	2129
31.44.2.1.10	Method 10:	Transesterification of Arylphosphonous Diesters	2130
31.44.3	Product Subclass 3: Amino(aryl)phosphines and Diamino(aryl)phosphines		2131
31.44.3.1	Synthesis of Product Subclass 3		2131
31.44.3.1.1	Method 1:	Reaction of Aryl(halo)phosphines and Aryl(dihalo)phosphines with Amines	2131
31.44.3.1.1.1	Variation 1:	With Silylamines	2132
31.44.3.1.2	Method 2:	Reaction of Diamino(chloro)phosphines with Aryl Grignard or Organolithium Reagents	2133
31.44.3.1.3	Method 3:	Reaction of Arylphosphonites with Amines	2134
31.44.3.1.4	Method 4:	Cleavage of the P—P Bond of Diphosphines and Related Compounds	2135
31.44.3.1.5	Method 5:	Addition of Amines to Aryl(imino)phosphines	2135
31.44.3.1.6	Method 6:	Amino Interchange of Amino and Diaminophosphines	2136
31.44.4	Product Subclass 4: Alkoxy(aryl)(halo)phosphines and (Alkylsulfanyl)(aryl)(halo)phosphines		2136
31.44.4.1	Synthesis of Product Subclass 4		2136
31.44.4.1.1	Method 1:	Friedel–Crafts Reaction	2136
31.44.4.1.2	Method 2:	Reaction of Aryl(dihalo)phosphines with Alcohols and Thiols	2137
31.44.4.1.3	Method 3:	Reaction of Aryl(dihalo)phosphines with Epoxides	2137
31.44.4.1.4	Method 4:	Interchange Reaction between Aryl(dihalo)phosphines and Arylphosphonous Diesters	2138
31.44.4.1.5	Method 5:	Reaction of Arylphosphonous Diesters with Halogens or Hydrogen Halides	2138
31.44.5	Product Subclass 5: Amino(aryl)(halo)phosphines		2139
31.44.5.1	Synthesis of Product Subclass 5		2139
31.44.5.1.1	Method 1:	Friedel–Crafts Reaction	2139
31.44.5.1.2	Method 2:	Reaction of Aryl(dihalo)phosphines with Amines	2139
31.44.5.1.3	Method 3:	Reaction of Diamino(aryl)phosphines with Phosphorus Trihalides	2141
31.44.5.1.4	Method 4:	Halogen Exchange of Chlorophosphines	2141
31.44.5.1.5	Method 5:	Cleavage of the P—P Bond of Diphosphines	2142
31.44.5.1.6	Method 6:	Addition of Hydrogen Halides to Aryl(imino)phosphines	2142
31.44.6	Product Subclass 6: Alkoxy(amino)(aryl)phosphines and (Alkylsulfanyl)(amino)(aryl)phosphines		2143
31.44.6.1	Synthesis of Product Subclass 6		2143
31.44.6.1.1	Method 1:	Reaction of Alkoxy(aryl)(halo)phosphines with Secondary Amines	2143
31.44.6.1.2	Method 2:	Reaction of Amino(aryl)(halo)phosphines with Alcohols	2143
31.44.6.1.3	Method 3:	Partial Alcoholysis of Diamino(aryl)phosphines	2144
31.44.6.1.4	Method 4:	Addition of Alcohols to Aryl(imino)phosphines	2145
31.44.6.1.5	Method 5:	Transamidation of Alkoxy(amino)phosphines	2145

Keyword Index	2155
Author Index	2203
Abbreviations	2269